

AL/EQ-TR-1993-0009

Vol I of V



AIR FORCE SITE CHARACTERIZATION AND ANALYSIS PENETROMETER SYSTEM (AFSCAPS): LASER-INDUCED FLUORESCENCE CONE PENETROMETER - SYSTEM DEVELOPMENT AND EVALUATION (VOL I OF V)

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December 1994

Final Technical Report for Period March 1992 - November 1992

Approved for public release; distribution unlimited.

19950519 017

DTIC QUALITY INSPECTED 5

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT Available for public release. Distribution unlimited.		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 5735			5. MONITORING ORGANIZATION REPORT NUMBER(S) AL/EQ-TR-1993-0009 Vol I of V		
6a. NAME OF PERFORMING ORGANIZATION Applied Research Associates, Inc.		6b. OFFICE SYMBOL (If applicable) ARA		7a. NAME OF MONITORING ORGANIZATION Air Force Civil Engineering Support Agency	
6c. ADDRESS (City, State, and ZIP Code) RFD #1, Box 120-A, Waterman Road South Royalton, VT 05068			7b. ADDRESS (City, State, and ZIP Code) HQ AFCEA/RAVW Tyndall Air Force Base, FL 32403-6001		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Armstrong Laboratory		8b. OFFICE SYMBOL (If applicable) EQW		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F08635-88-C-0067	
8c. ADDRESS (City, State, and ZIP Code) 139 Barnes Drive, Suite 2 Tyndall AFB FL 32403-5323			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
11. TITLE (Include Security Classification) Air Force Site Characterization and Analysis Penetrometer System (AFSCAPS); Laser-Induced Fluorescence Cone Penetrometer, Volume I - System Development and Evaluation (Vol. I of V)					
12. PERSONAL AUTHOR(S) James D. Shinn, Wesley L. Bratton, Greg Gillispie, Randy St. Germain					
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM <u>Mar '92</u> TO <u>Nov '92</u>		14. DATE OF REPORT (Year, Month, Day) December 1994	
15. PAGE COUNT					
16. SUPPLEMENTARY NOTATION Approved for Public Release. Distribution unlimited. AL/EQW Project Manager: Bruce Nielsen; DSN 523-6227; commercial (904) 283-6227					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	fluorescence, characterization, development, demonstration, cone penetrometer, soil, groundwater, BTEX, fuels		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A prototype Laser-Induced Fluorescence-Electronic Cone Penetrometer Test (LIF-CPT) system was demonstrated at Tinker Air Force Base (Tinker AFB), Oklahoma as an innovative technology for delineating soil contamination resulting from fuel spills. Applied Research Associates, Inc. (ARA) and North Dakota State University conducted the development program for the Air Force using LIF-CPT components developed within the Tri-Service Site Characterization and Analysis Penetrometer System (SCAPS) effort. Major components of the system consisted of ARA's cone penetrometer system coupled with North Dakota State University's tunable laser fluorimeter. To enable rapid, efficient and minimally invasive site characterization, the LIF-CPT probe data output was linked to ARA's real-time analysis system with three-dimensional modeling and scientific visualization capabilities. Field testing at Tinker AFB was conducted to evaluate the LIF-CPT probe. During the testing program, 112 soundings at 8 contaminated sites were conducted. At select locations, soil and water samples were obtained with CPT or drilling technologies, and tested using analytical procedures to confirm the presence of fuel contamination. These results allowed the detection limits of the LIF-CPT probe to be evaluated for jet fuels. The Tinker AFB demonstration indicates that the LIF-CPT system can detect TPH concentrations to at least 100 mg/kg. the lower bound detection limit is believed to be lower than 100 mg/kg, but scatter in the analytical and LIF data precluded accurate determination of this bound. Research planned for the summer of 1993 will address determining the LIF-CPT lower bound detection limit.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL Bruce Nielsen			22b. TELEPHONE (Include Area Code) (904) 283-6011		22c. OFFICE SYMBOL RAVW

DD Form 1473, JUN 86

Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
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PREFACE

This report was prepared by Applied Research Associates, Inc. (ARA), Waterman Road, South Royalton, VT 05068, under contract FO8635-88-C-0067, SETA SSG Subtask 8.00, for the Air Force Civil Engineering Support Agency, Engineering and Services Laboratory, Tyndall Air Force Base, Florida 32403-6001. North Dakota State University was a subcontractor to ARA and fabricated and assisted in demonstrating the laser spectrometry technology.

This work was sponsored by the Oklahoma City Air Logistics Command, Directorate of Environmental Management (OC-ALC/EM) and the U.S. Air Force Civil Engineering Support Agency (AFCEA). Ms. Beverly Allen of OC-ALC/EM and Mr. Bruce Nielsen of AFCEA/RAVW were the Government technical program managers.

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Unannounced	<input type="checkbox"/>
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Availability Codes	
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EXECUTIVE SUMMARY

A. OBJECTIVE

The Air Force Site Characterization and Analysis Penetrometer System (AFSCAPS) project was initiated to further develop the combined technology of the U.S. Army Corps of Engineers Waterways Experiment Station's (WES) SCAPS program and the Air Force Laser Spectroscopy Program. The purpose of the program was to enable the Air Force to address characterization, remediation and post-remedial monitoring of fuel-contaminated sites in a more efficient and effective manner. The primary objectives of this program were to develop, demonstrate, and evaluate the Laser-Induced Fluorescence-Cone Penetrometer Technique (LIF-CPT) system for the characterization of petroleum fuel-contaminated sites.

B. BACKGROUND

The Department of Defense is conducting nationwide remediation efforts to clean up contaminated military and weapons facilities. It has been estimated that remediation of these DoD facilities will require expenditure of \$24 billion dollars by the DoD over the next 30 years. Identifying, characterizing and developing remediation plans for these contaminated sites is a high priority for the DoD.

Potential cost savings realized through cone penetrometer-based environmental site investigations have fostered federal research and development efforts by the U.S. Army, Navy and Air Force. Together they have supported the Tri-service Site Characterization and Analysis Penetrometer System (SCAPS) program. To better characterize hazardous waste sites, improved investigative tools and methods are being developed for use with cone penetrometers. One such tool is the laser fluorimeter. Initially developed at WES, specifically for use in detecting diesel fuel marine (DFM) for the U.S. Navy, the Air Force has sponsored additional research to modify the laser fluorimeter/cone penetrometer system for use in detecting jet fuel, heating oil and gasoline-contaminated soils.

C. SCOPE

To accomplish the objectives of this project the following tasks were completed:

- ◆ evaluation of the current LIF state-of-art,
- ◆ development of specifications for the new LIF system,
- ◆ fabrication and laboratory testing/evaluation of the LIF-CPT system,
- ◆ field demonstrations and evaluations at Tinker and Carswell AFBs of the AF LIF-CPT system.

This technical report is organized in five separate volumes:

- ◆ Volume I discusses the development of the LIF-CPT system including a review of the current state-of-art of the WES SCAPS program and NDSU's research work.
- ◆ Volume II is a review of the sites investigated at Tinker AFB.
- ◆ Volume III presents results from Carswell AFB.

- ◆ Volume IV consists of comprehensive appendix of all LIF-CPT logs, boring logs, WTM plots, and demonstration, test and evaluation (DT&E) plans for both Tinker and Carswell AFB's.
- ◆ Finally, Volume V contains the laboratory analytical data for samples obtained at Tinker AFB.

D. METHODOLOGY

The WES system employed a nitrogen laser system that is limited to the emission of a single excitation wavelength of 337 nanometers (nm). This is useful for the detection of large multi-ring fuels such as DFM but it has been shown that light fuels such as jet fuels and gasoline have only weak spectral signatures when excited with a 337 nm light pulse. Excitations at shorter wavelengths, such as 280 to 290 nm for jet fuels and 260 nm for gasoline, provide much stronger and distinctive fluorescence spectra. One of the primary goals of this project was to develop and test a tunable laser that allows the investigator to select the most appropriate wavelength depending on the contaminant of interest and site conditions.

Under this program, North Dakota state University (NDSU) developed and tested a laser fluorimeter to analyze aromatic hydrocarbons in situ. The NDSU system features a full-wavelength tunable dye system with a pulsed laser (Nd:YAG), fiber optic probe and detection system. Applied Research Associates, Inc. (ARA) incorporated the laser system with a cone penetrometer truck producing a robust site assessment tool capable of quickly locating and quantifying fugitive petroleum, oil and lubricant (POL) contamination.

E. TEST DESCRIPTION

The test program consisted of two phases, (1) evaluation of the LIF-CPT probe under laboratory conditions, and (2) evaluation of the LIF-CPT probe under field conditions.

The laboratory testing consisted of three major efforts (1) selecting and characterizing representative soils from Tinker AFB, (2) evaluation of the effect of bending the fiber-optic cable on the LIF response, and (3) determining the sensitivity of the LIF system to expected fuel contaminants.

During the field demonstration and evaluation program several objectives were addressed. Primarily, this phase demonstrated that a CPT deployed LIF system could be used to locate fuel-contaminated soils to at least the regulatory limits of 100 ppm. Other criteria such as system reliability, stability and repeatability, correlation of LIF-CPT intensity to contaminant concentration and evaluation of the sources of data scatter in the chemical and LIF-CPT data were evaluated. In addition, the cost effectiveness of the LIF-CPT was evaluated as well as its ability to provide highly detailed real-time data for on-site graphical representation.

F. RESULTS

The following summarizes the results from the laboratory and field evaluations:

- ◆ Attenuation due to bending in the fiber optic cable was not significant except at the probe end where the fibers are bent 90 degrees in a 1.25 inch radius. High mechanical stresses caused the glass fibers to separate from the nylon jacket and move relative to the focal plane resulting in unacceptable baseline levels.
- ◆ The fluorescence spectra of JP-4 and JP-5 were indistinguishable using the LIF-CPT system. The WTM's of jet fuel and heating oil were noticeably different.
- ◆ Fluorescence of PAHs dominate the emission spectra of the subject fuels for excitation in the ultraviolet region shorter than 300 nm. The optimal excitation wavelength for continuous LIF-CPT soundings is 280-290 nm or shorter.
- ◆ The variation in the fluorescence spectral distribution is dependent on the matrix (i.e., neat, dissolved, on soil).
- ◆ Humic acids' contribution to LIF in soils play an important role in the long wavelength fluorescence spectral distribution.

G. CONCLUSIONS

Evaluation of the AFSCAPS at Tinker AFB demonstrated that the combination of an LIF-CPT, onsite analytical laboratory, and onsite three-dimensional visualization software can provide more detailed and timely mapping of fuel contamination than can be accomplished by conventional drilling and sampling programs. The LIF-CPT can provide a continuous profile of the contaminant location and relative concentration with detection levels to at least the regulatory limits for TPH.

H. RECOMMENDATIONS

A two-pronged approach is recommended for future development of the LIF-CPT. One aspect should be the continuation of the field studies to provide a broader database for further evaluation of the LIF-CPT probe in a wider range of geologic settings. The other aspect should include improvements in instrumentation, and laboratory and field methods in order to establish the bias, reproducibility, and error of the LIF-CPT system for regulatory acceptance.

I. APPLICATION

The LIF-CPT system could be implemented by the Air Force as the primary technology to conduct environmental site assessments where petroleum, oils and lubricants are involved.

J. BENEFITS

This technology could significantly reduce the time / cost of conducting site assessments and provide superior data to use as a basis for choosing an appropriate remedial strategy.

K. TRANSFERABILITY OF TECHNOLOGY

Virtually all industrial contractors involved with subsurface environmental site assessments where petroleum oils and lubricants are concerned could profit from the use of LIF-CPT technology. The industry in general is constantly seeking ways to conduct business faster, cheaper, and better; CPT-LIF fulfills these criteria.

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SECTION I

INTRODUCTION

A. OBJECTIVE

The Air Force is seeking efficient means to assess, remediate, and monitor petroleum-contaminated and hazardous waste sites at both active and decommissioned installations. Contaminated sites found at Air Force bases include those caused by fuel spills incurred during daily base operations. Jet fuels such as JP-4, JP-5 and JP-8 are the most common fuels to be stored, transferred and consumed, although other fuel spills such as heating oil and gasoline are also of concern to the Air Force. Typical jet-fuel-contaminated sites at Air Force installations include fuel storage and transfer facilities, fuel purge areas, and firefighter training facilities. The Air Force's Installation Restoration Program Information Management System (IRPIMS) database lists approximately 1,400 fuel-contaminated sites and 300 inactive firefighter training facilities; the IRPIMS database contains data from only one-half of the installations.

To better characterize hazardous waste sites, improved investigation tools and methods are being developed that use cone penetrometers. Cone penetrometer testing gathers high-quality in situ geotechnical information in a rapid and cost-effective manner. Moreover, in situ geophysical and chemical sensors adapted to the cone penetrometer probe enable mapping of subsurface contamination in sufficient detail to reduce the number of costly and invasive subsurface sampling and monitoring wells needed. Compared to cone penetrometer technology, traditional drilling methods have high waste management costs resulting from handling and disposing of contaminated soils extracted as drilling waste. In addition, cone penetrometer testing minimizes exposure of field personnel to hazardous environments, unlike drilling where the bore hole is open to the atmosphere.

Potential cost savings of penetrometer-based environmental site investigations have fostered federal research and development efforts. Subsequently, the Army, Navy and Air Force have supported the Triservice Site Characterization and Analysis Penetrometer System (SCAPS) program which has been conceived and directed by the U.S. Army Corps of Engineers

Waterways Experiment Station (WES). The work at WES has focused on diesel fuel marine (DFM), which is heavier than the fuels of interest to the Air Force. To supplement the SCAPS work at WES, the Air Force has sponsored additional work under the Laser Spectroscopy Program. Under this program, North Dakota State University (NDSU) has developed and tested a laser fluorimeter to analyze aromatic hydrocarbons in solution, neat fuel, and fuel dissolved in water. The NDSU system features a full-wavelength tunable dye laser with a pulsed laser (Nd:YAG), fiber optic probe and detection system. This system provides excitation wavelengths shorter than the nitrogen laser system used by WES in the SCAPS program. With the shorter excitation wavelengths, the lighter fuels such as jet fuels and gasoline can be excited and detected.

The Air Force Site Characterization and Analysis Penetrometer System (AFSCAPS) project was initiated to rapidly develop the combined technology of the SCAPS program and the Air Force Laser Spectroscopy Program. This work was accomplished by installing the NDSU laser system in an Applied Research Associates, Inc. (ARA) cone penetration vehicle and implementing the system using the fiber optic cone concept from WES. The objective of the program was to develop, demonstrate, and evaluate the Laser Induced Fluorescence-Cone Penetrometer Technique (LIF-CPT) system for the characterization of fuel contaminated sites. Jet fuels were the primary interest, although limited testing of heating oil and gasoline contaminated soils was conducted. The LIF-CPT was used in a 30 day field demonstration program at Tinker AFB to gather data for system evaluation. This volume describes the LIF-CPT system that was assembled and used during the demonstration program. The results are used to evaluate the utility of the LIF-CPT system and make recommendations for use and further development of the system.

B. BACKGROUND

Laser-Induced Fluorescence (LIF) technology as applied to the environmental field is relatively new, with the first published work conducted by Hirschfeld, et al. (2) and Chudyk, et al. (3), followed shortly thereafter by Gillispie and St. Germain (4), Lieberman, et al. (5), and others. The initial work and much of the current work is centered on developing a field-portable

LIF system that can be used in monitoring wells to supplement and, in the future, replace analytical testing. Research in this field has demonstrated the fluorescence characteristics of a wide range of chemical compounds. Common chemical contaminants such as the chlorinated hydrocarbons (TCE, PCE) are known not to fluoresce and are not a candidate for the LIF technique. As demonstrated by Gillispie and St. Germain (4), Lieberman, et al (5), and Chudyk, et al (3), common fuel contaminants such as heating oil, jet fuels, gasoline, and diesel fuel marine exhibit strong fluorescence signatures, with the degree of fluorescence depending on the excitation wavelength. Large multiring fuels such as DFM will fluoresce with long wavelength excitation sources such as the 337 nanometer (nm) nitrogen laser used in the SCAPS system. Lightweight fuels such as jet fuels and gasoline have only weak or non-existent spectral signatures when excited with a 337 nm light pulse. Excitations at lower wave lengths, such as 280 to 290 nm for jet fuels and 260 nm for gasoline, provide much stronger and distinctive fluorescence spectra. However, a severe limitation of this shorter wavelength excitation is the increased light attenuation as compared to the longer wavelength 337 nm laser. A tunable laser, as demonstrated on this project, allows the investigator to select the most appropriate wavelength depending on the contaminant of interest and site conditions. This was the motivating force behind the NDSU laser system.

C. SCOPE/APPROACH

The two main objectives of this project were: (1) to develop a state-of-art LIF-CPT system for detection and characterization of fuel contaminated sites, and (2) to demonstrate and evaluate this system at typical Air Force sites. To accomplish these objectives, the project was divided into the following tasks: (1) evaluation of the current state of art, (2) develop specifications for the LIF system, (3) fabrication of the system, (4) laboratory evaluation tests and Demonstration Test and Evaluation Plans for Tinker and Carswell, and (5) field demonstrations and evaluations at Tinker AFB and Carswell AFB. A summary of the work accomplished under each task during the 8-month project period are outlined below:

1. Demonstration Program at Tinker AFB, Oklahoma and Carswell AFB, Texas: Conduct a comprehensive 30-day DT&E field program at Tinker AFB. Perform operational testing of optical cone penetrometer technology for fuel-contaminated sites and demonstrate related

AFSCAPS technologies. Perform sampling and analyses at various sites with known or suspected JP-4 jet fuel, fuel oil, heavy metal, volatile or semivolatile organic compound contamination. Perform two-day demonstration with the cone penetrometer and laser spectrometer at fuel-contaminated sites.

2. Demonstration, Testing and Evaluation Plan: Develop demonstration work plans for field activities at contaminated sites at Tinker AFB, Oklahoma, including sampling and analysis plans and health and safety plans. Provide plans for a Carswell AFB, Texas demonstration as well.

3. Laboratory Validation: Conduct laboratory testing to evaluate the LIF spectrometer system performance on soils. Assess the specificity capabilities of the LIF using lifetime and multi-dimensional LIF data. Perform bench-scale testing of the assembled instrumentation.

4. Technology Acquisition and Fabrication: Specify and fabricate the Laser Induced Fluorescence - Cone Penetrometer Technique system for operational testing, and install the equipment in one of ARA's cone penetrometer vehicles.

5. Technology Review: Review of Tri-Service SCAPS and Air Force Laser Spectroscopy programs; identify and obtain specifications of technology to be integrated as part of this project.

Similar to WES's SCAPS program, the goal of the emerging AFSCAPS program is to enable the Air Force to address characterization, remediation and postremedial monitoring of Air Force fuel-contaminated sites in a more efficient, safe and effective manner. The development of LIF spectroscopy for the cone penetrometer is but one of the possible AFSCAPS technologies. Implicit within the AFSCAPS program objectives are developments relating to onsite data analysis. Real-time and in situ cone penetrometer data are collected and processed, and ideally combined into three-dimensional modeling packages that allow visualization of the results. Visualization of LIF and chemical distribution was successfully demonstrated during the field program.

Figure 1 shows the major hazardous waste sites listed by Tinker AFB's Directorate of Environmental Management. Six of the seven sites investigated in the DT&E (North Tank area, Fuel Purge area, Industrial Wastewater Treatment Plant, Soldier Creek, Landfill 4, and Landfill 2) are shown in Figure 1. The seventh demonstration site, Fire Training Area 3, is located adjacent to Fire Training Area 2 in Figure 1. Most of the sites studied are included within the Air Force Installation Restoration Program (IRP), with one site, the North Tank Area, being an operable unit of the Building 3001 NPL site.

Several of the test areas were targeted for operational testing and evaluation of the LIF-CPT probe. Tip stress, sleeve friction and pore pressure were measured in real-time to classify soil type as a function of depth. LIF intensity with depth was plotted in real-time as well. ARA's mobile gas chromatography (GC) laboratory and an off-site certified laboratory performed analytical tests on soil and water samples for comparison to the in situ LIF results.

An extensive soil and water sampling and testing program was carried out in addition to the LIF-CPT technology demonstration. Depending on the particular site, the sampling and analysis was used to characterize the nature and extent of Total Petroleum Hydrocarbons (TPH), volatile organic and semi-volatile organic compounds, and metals. Each site investigation generally involved site reconnaissance mapping and surveying, LIF-CPT profiling, soil sampling using the CPT and drill rig, water sampling from CPT and open drill holes, onsite gas chromatography, and off-site analytical testing. Waste management, decontamination procedures, and grouting were performed as part of the program as well.

As part of the AFSCAPS demonstration, LIF-CPT data were transferred to a Silicon Graphics workstation for onsite analysis. Relational database, statistical modeling and visualization software were implemented to produce three-dimensional images of LIF intensity. Visualization of LIF results at two fuel-contaminated sites (North Tank Area; Fuel Purge Facility turn-around area) illustrated the lateral and vertical extent of contamination.

Figure 1. Photograph of Tinker AFB Showing Layout of the Base and Major Hazardous Waste Sites

Results from the demonstration at Tinker AFB also provided data on the subsurface hydrogeologic and contaminant types at each of the above sites. This data will aid Tinker environmental management staff and regulators in preparing final environmental assessments and/or remedial investigations/feasibility studies for the respective sites.

D. ORGANIZATION

The technical report is organized in five volumes, with Volume I discussing development of the LIF-CPT system. Within Volume I, Section II provides a review of the current state-of-art of the WES SCAPS program and NDSU's research work under the Air Force Laser Spectroscopy program. Section III contains a description, function and operation of the component hardware comprising the LIF-CPT probe. Section IV summarizes the laboratory testing performed to assess the influence of various parameters on the LIF signal for calibration purposes. Although advances were made in our understanding of the source and response factors for LIF-CPT measurements, many additional questions were raised which could not be fully addressed in this project. Included in Section V are detailed analyses of the LIF-CPT data and development of correlations to contaminant levels. Section VI contains conclusions and recommendations regarding the LIF-CPT system.

Presented within Volume II is a review of sites investigated at Tinker AFB site. Site plans, representative LIF-CPT logs, LIF multidimensional analyses, cross-sections, and three-dimensional graphics are presented and discussed on a site-by-site basis. Conclusions regarding each of the sites investigated at Tinker AFB are contained in Volume II. Volume III presents results from Carswell AFB and is organized in a format similar to Volume II.

All LIF-CPT logs, CPT-derived soil logs, boring logs, WTM plots, and DT&E plans are provided in the appendices of Volume IV. Volume V contains the laboratory analytical data for samples obtained at Tinker AFB.

SECTION II

TECHNOLOGY REVIEW

A. INTRODUCTION

Fiber optic spectroscopy is a promising tool for in-situ analysis of fuels, solvents, and other chemical species. The two main categories of fiber-optic spectroscopy are direct methods in which the fiber functions essentially as a "light pipe," and fiber optic chemical sensors (optrodes) in which interaction between an analyte and a reagent immobilized on the fiber affects the light signal passing through the fiber.

In this section, a review of the state-of-the-art of environmental analysis via Laser-Induced Fluorescence (LIF) with fiber-optic probes is made. The review covers the time up to the beginning of this project (May 1992) and is specifically limited to: (1) the detection and determination of petroleum hydrocarbon components in water and soil matrices using fluorescence spectroscopy, (2) in situ measurements using LIF fiber-optic probes, and (3) the merger of such technology with the cone penetrometer.

Accordingly, this section outlines the principles of LIF measurements and the most important hardware and software options. Fiber-optic spectroscopy technology developed by the Waterways Experiment Station (WES) within the Triservice Site Characterization and Analysis Penetrometer System (SCAPS) program is reviewed. Alternative excitation, detection, and signal processing schemes and their applicability to the characterization of fuel-contaminated sites found at Air Force bases are presented. The laser system designed and built at North Dakota State University (NDSU) as part of the Air Force Laser Spectroscopy Program addresses these field screening needs.

B. PRINCIPLES OF LASER-INDUCED FLUORESCENCE (LIF)

Fluorescence is the most familiar of several luminescence (light emission) processes, including phosphorescence, chemiluminescence, bioluminescence, and triboluminescence. Their

unifying feature is that photons are emitted simultaneously with the transition of an excited atomic or molecular species to a lower energy state. Not all materials are luminescent since there are additional molecular deactivation pathways to light emission. For the present purpose, it is assumed that the fluorescence occurs from molecules that have been electronically excited by light absorption. Fluorescence is distinguished from phosphorescence by the timescale of the emission (fluorescence usually occurs within microseconds or less following the excitation, whereas the phosphorescence emission extends over a longer time period) and from the other luminescence in the means by which the excitation is created. In both chemiluminescence and bioluminescence, the molecular excitation is created during reactions that yield high energy. Bioluminescence means that the reactions are of a biological nature. Mechanical impact is the source of the excitation in triboluminescence.

The features common to fluorescence experiments are: a light source to induce the photoexcitation process, optics to deliver excitation light from source to sample, optics to deliver emitted fluorescence from sample to detector, detector to convert the light signal into an electrical signal, and further signal processing. General comments about each of these features follow:

1. Light source - The light source must provide sufficiently short wavelength photons (energy of the photons increase as the wavelengths decrease) to be able to excite the analytes of interest. For example, the BTEX components of JP-4 jet fuel require excitation photons with wavelengths of about 300 nm or shorter. The light source could be a continuous laser, a pulsed laser, or an incoherent source such as a mercury or xenon arc lamp. An important design issue is whether the light source is tunable (wavelength-selectable) or at fixed wavelength.

2. Source to sample delivery optics - Remote spectroscopy relies on fiber optics to deliver the excitation light to the sample. Because fiber optic diameters are typically less than 1 mm, lasers have substantial advantages over incoherent sources in terms of the optical power that can be delivered to the sample. Only lasers will be considered in the rest of this discussion. The degree to which light is attenuated as it travels along the fiber is a function of wavelength. The rate at which the light energy is attenuated increases as the wavelength decreases.

3. Sample to detector collection optics - The fluorescence emitted by individual molecules can be considered to take place with an isotropic distribution. With increasing number and diameter of the collection fibers, more light will be delivered to the detector. One of the important trade-offs is fiber cost versus light collection efficiency. The cost of a 50-meter long fiber optic probe could easily range from as low as \$500 to as much as \$10,000. The lower cost would be represented by a probe with a single collection fiber of relatively small diameter (approximately 250 micrometer [μm]) plastic-clad silica, whereas the expensive probe would use six collection fibers of large diameter (600 μm) silica-clad silica fiber. Many factors must be considered in selection of the most cost-effective approach.

4. Detector - The detector converts the fluorescence photons presented to it into an electrical signal. The usual spectral presentation is a plot of intensity versus emission wavelength. The wavelength resolving device is generally a monochromator, which employs a diffraction grating or prism to effect a spatial separation of the light. The typical arrangement relies on a slit to select a narrow wavelength range of the dispersed emission for conversion to a current or voltage by the photomultiplier tube. This experiment can be repeated many times at different wavelengths to generate the full spectrum. Recent advances in array detector technology, such as optical multichannel analyzers (OMA) and charge-coupled device (CCD) detectors, has made it possible to collect the entire spectrum at once, speeding up the data collect time significantly.

5. Signal processing - If the excitation source is continuous, the options for signal processing are limited essentially to a fluorescence intensity versus wavelength. With pulsed excitation the options are greater. The time profile over which the fluorescence is emitted depends on the excitation pulse duration, the chemical identity of the sample, and any temporal distortion introduced by the signal collection and processor instrumentation. Examination of the time profile can form the basis of improved detection specificity, i.e., the ability to distinguish the chemical identity of the emitting molecules. The combination of a photomultiplier tube with a digital oscilloscope directly provides the emission time profile (albeit at a single emission wavelength). To acquire the temporal information with an OMA or CCD detector, the technique of "gating" is required. In gating, the supply voltage to the detector is "on" for only a selected interval and at a selected delay after the photoexcitation. Recording of the spectrum as a

function of the delay in a discrete series of experiments generates the full time profile. In either the phototube-digital oscilloscope or gated OMA/CCD approaches, one ultimately can generate a "wavelength-time matrix" (WTM), a multidimensional data presentation with emission wavelength along one axis, emission time along another, and intensity along a third axis.

C. AFSCAPS BACKGROUND

The Air Force Site Characterization and Analysis Penetrometer System is an outgrowth of the Tri-Service SCAPS program established by the U.S. Army Corps of Engineers Waterways Experiment Station and was discussed in Section I of this report. The centerpiece of the SCAPS is the cone penetration technology. As discussed in Reference 1 and summarized in Table 1, the CPT-based environmental characterization system has a number of advantages over conventional drilling and sampling programs. As part of WES's program in this area the LIF-CPT probe was developed.

The essence of the WES LIF-CPT idea was to incorporate a sapphire window in the side of the cone such that light could be directed from inside the cone onto the soil moving past the sapphire window as the cone is pushed into the ground. The light that is directed onto the soil is chosen to contain the appropriate wavelength(s) to excite fluorescence of petroleum contaminants on the soil. Fluorescence back scattered into the cone is collected by a fiber optic cable, which returns the light to the surface for quantitation. Originally, WES positioned a mercury lamp "downhole" in the cone as the excitation source, but soon began to use a laser located in the CPT truck as the source. Light from the laser is directed from the truck into the cone with a second optical fiber. Both the delivery and collection fibers are bundled into the instrumentation cable with the other conventional geotechnical sensors.

TABLE 1. TRISERVICE SCAPS STRENGTHS AND LIMITATIONS

U.S. Army Corps of Engineers (Reference 1)

Strengths
Screens for chemical contamination characteristics using electrical resistivity and optical properties of soil
Determines soil type from strength data
Includes surface geophysical scanning to detect obstacles/hazards
Allows sealing and grouting of penetrometer holes
Saves time and money over conventional drilling
Minimizes crew's exposure to hazardous materials
Allows for decontamination of surfaces and compartments exposed to hazardous wastes
Integrates data into unified databases
Samples soil and groundwater
Collects real-time data and allows partial onsite interpretation
Provides on-site visualization of subsurface conditions
Installs monitoring/sampling devices
Limitations
Cannot be used in competent rock or cemented soils without pre-drilling
Sensors provide only qualitative to semi-quantitative measurement of contaminant concentration
Sensors identify classes of compounds only
Soil and water samples are typically smaller than those provided by drilling

The fiber-optic approach described in the previous paragraph is necessarily a direct one. Optrodes are more difficult to implement on a cone penetrometer for two reasons. First, they require intimate contact between the sensing device and the sample. Second, they cannot respond fast enough to allow concentration profiles to be measured during a push. The principal direct fiber-optic spectroscopies are near-IR and UV absorption, fluorescence, and Raman scattering. This review emphasizes fluorescence measurements, since fluorescence is the only spectroscopic measurement teamed to date with the cone penetrometer technology, but the experimental approach to Raman scattering would be very similar. Absorbance techniques may be of some value for groundwater measurements, but are too insensitive for detection of contaminants on soil.

D. THE WES IMPLEMENTATION OF OPTICAL CONE PENETROMETER

The main components of the laser system installed in the WES cone penetrometer are the nitrogen laser excitation source, the fiber-optic light delivery and collection probe, and optical multichannel analyzer (OMA) detector. Each of these is briefly summarized below.

1. Laser Source

The excitation source is the Model PL2300 nitrogen gas laser manufactured by Photon Technology International (PTI). Nitrogen lasers are single wavelength gas discharge devices that provide pulsed output in the near-ultraviolet at 337.1 nm. The PL2300 is rated at 1.4 megajoules/pulse (mJ/pulse) energy delivered over a pulse of approximately 600 ps (0.6 ns) duration. It is of the type known as a TEA (Transverse Excitation at Atmospheric pressure) laser, which is advantageous for this application because no vacuum pump is required. An external gas supply (nitrogen cylinder) is necessary and gas consumption is high; a standard nitrogen cylinder is exhausted in approximately 6 hours of actual running time. The PL2300 can be operated at a repetition rate of up to 20 Hz (pulses per second), but WES finds that the laser stability is better at 10 pulses/second. Using this system, WES is able to obtain pulse durations of just under 1 ms/pulse.

WES is exploring use of a Nd:YAG laser and harmonic generator accessory from Continuum, which provides pulsed light at 355 nm (third harmonic) and 266 nm (fourth harmonic). They hoped to take advantage of the multiple wavelength output, the possibility of deeper UV excitation (< 300 nm wavelength), and more intense light output. The main difficulty they have encountered in using the ND:YAG laser is frequent catastrophic damage to the launch fiber.

2. Fiber-Optic Probe

Optical cone penetration technology requires a delivery fiber to bring light from the laser source to the cone and one or more collection fibers to return fluorescence (or Raman

scattered light) from the sample back to the detector. The WES arrangement relies on a single collection fiber of the same type as is used for light delivery. This Ensign-Bickford fiber has a fused silica core of 360 micrometers diameter, fused silica cladding, and Tefzel® buffer. The cost is approximately \$15 per meter.

At the probe, the collection and delivery fibers terminate flush with the face of a circular aluminum mount that has an outside thread. The holes in the mount through which the fibers pass are angled at approximately 11 degrees to improve overlap of the delivery and collection cones. When the probe is fully assembled the fiber ends are approximately 2 mm from the inner face of the sapphire window.

The 1/4-inch diameter sapphire window is positioned in the side of the cone approximately 2 feet above the tip. A 1/4-inch wide flat is milled for several inches to either side of the window on a line parallel to the cone axis to bring the outside face of the window flush with the cone. The window itself is epoxied into a circular ring with a inside threaded projection. As the ring, resting on a shoulder, is rotated with a spanner wrench, its inside thread mates with the outside thread of the disk holding the fibers and "snugs" it into a predetermined position.

WES has not experienced major difficulties with the sapphire windows except in gravels where the sapphire window has broken*. They feel that "smearing" associated with the cone passing through a contaminant plume is not a problem, i.e., the window is rapidly scoured during a push. Their evidence is that as they pass from one soil stratum contaminated with product into a clean one, the fluorescence signal does not tail off, but instead ends abruptly.

3. Data Acquisition

WES uses an optical multichannel analyzer (OMA) detector (Model 1463, manufactured by Princeton Research). The OMA can acquire the full wavelength distribution

* Personal communication from P. Malone of WES to J. Shinn of ARA at Tinker AFB, September 1992.

As mentioned previously, the nitrogen laser is fired 10 times per second. Current practice is to accumulate and average 10 laser shots per data point. Therefore, a fluorescence spectrum is downloaded every second. At the standard push rate for the cone, this corresponds to a spatial resolution of about 2 cm.

E. ANALYTICAL SPECTROSCOPY CONSIDERATIONS

A major challenge for field application of fiber-optic fluorescence spectroscopy is speciation capability. In principle, one could measure the emission with a fixed wavelength source and decompose the spectrum into its individual components by a partial least squares fit of the type used for near-IR absorption. Unfortunately, the breadth of polycyclic aromatic hydrocarbons (PAH) fluorescence spectra and the lower signal-to-noise ratio (relative to absorption) suggests this approach is only viable for monitoring situations where the contaminant identities are already known or suspected. In field screening applications, the background from humic acid or the overlapping spectra of many contaminants are problematical. Additionally, the excitation from a single wavelength source, e.g., the nitrogen laser, may not be at the optimal wavelength for highest sensitivity of the chemical of interest. For example, the molar absorptivity of benzene at 266 nm (the Nd:YAG 4th harmonic wavelength) is lower by an order of magnitude from its value just 6 nm away at 260 nm.

Higher spectral dimensionality increases analysis specificity for multi-component samples. Absorption has a single experimental parameter (wavelength) and is therefore one-dimensional. Fluorescence is two-dimensional if the source is wavelength selectable. Pulsed excitation adds a third dimension, the time scale over which the fluorescence is emitted.

Fluorescence is a power spectroscopy, i.e., the detected signal intensity is proportional to the excitation flux. It is also ideally a zero-background experiment. In reality there is always some background (from physical scattering) but nonetheless, fluorescence usually represents small signals against an even weaker background. High source radiant power is therefore desirable, especially for ultraviolet work since fiber attenuation in this region is large. Background scattering will be more of a problem for studies of soils than for groundwater.

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F. ALTERNATIVES TO THE WES APPROACH

This section provides background for discussion of the many possible alternatives to WES's choices for excitation source, fiber optic material and configuration, detection electronics, and data processing algorithms.

1. Laser Source

The sensitivity of direct fluorescence analysis of polycyclic aromatic hydrocarbons is well established (References 2 and 3). The efficacy of tunable excitation has been demonstrated under laboratory conditions (Reference 4). They achieved sub-part-per-trillion detection limits for several PAHs with an apparatus based on a frequency-doubled pulsed tunable dye laser (nitrogen laser pumped).

A key element in any fluorescence measurement is the excitation light source. Lasers have obvious advantages over incoherent sources for direct fiber optic spectroscopy owing to the efficiency with which laser light can be launched into a fiber. Only laser sources are considered in this review. Laser fiber-optic fluorescence spectroscopy was introduced in Reference 2.

In principle, there is a choice between CW (continuous wave) and pulsed sources. The biggest limitation of CW lasers is that their strongest output lines are at wavelengths too long to excite the species of interest. Much environmental work is driven by the need to detect and analyze the single ring BTEX class (benzene, toluene, ethylbenzene, xylenes), which are the more water-soluble components of gasoline, JP-4 jet fuel, etc. The BTEX components require

excitation at wavelengths shorter than 280 nm but CW lasers can not excite aromatic compounds with fewer than three rings. Moreover, the CW lasers offer only discrete wavelengths and cannot provide fluorescence lifetime information. Fluorescence measurements with CW lasers are one-dimensional.

The pulsed source options include the nitrogen gas laser (337 nm output), Q-switched Nd:YAG (fundamental at 1064 nm, harmonics at 532, 355, and 266 nm) and rare gas/halogen excimer lasers (output at 351, 308, and 249 nm for XeF, XeCl, and KrF gas mixtures, respectively). All provide 1-10 nanosecond duration light pulses and are therefore suitable for fluorescence lifetime measurements. However, once the requirement of field operation is added, the excimer option becomes less attractive owing to the gas handling and water cooling requirements of high power versions. Nitrogen lasers are fairly inexpensive and simple in design. On the negative side, 337 nm is too long a wavelength to excite the fluorescence of the BTEX molecules, naphthalene, and other two-ring PAHs. The nitrogen laser is suitable for detection of diesel fuel, kerosene, and other more viscous, less refined fuels. In many ways the 4th harmonic of Nd:YAG at 266 nm offers the best combination of power, wavelength, beam quality, and robustness for a single frequency laser. On the other hand, light attenuation in the fiber increases sharply for wavelengths shorter than 300 nm and light transmission properties are likely the most crucial issue for probes longer than about 40 meters.

There are obvious attractions to a tunable (i.e., wavelength selectable) laser system. One can customize the excitation wavelength for the analyte(s) of interest if information about the site already exists. The ability to vary the excitation wavelength greatly enhances the opportunities for speciation (see next section). Detection limits and minimization of interferences are other benefits that could result.

The Kenny group at Tufts University has developed a quasi-tunable pulsed laser source by Raman shifting the Nd:YAG harmonics with hydrogen and/or methane gas mixtures. The result is a series of lines throughout the ultraviolet and visible at an average, albeit somewhat irregular, spacing of 5-10 nm. They then acquire non-time-resolved fluorescence spectra for each of these excitation wavelengths and assemble them into an excitation-emission

matrix (EEM) for least squares multicomponent analysis. Some promising results have been obtained for synthetic mixtures in the laboratory (Reference 5).

2. Fiber Optic Probe

One of the more crucial choices is whether to use fiber with silica cladding or plastic cladding. However, so many factors must be considered that there is not a single, unequivocal answer. The relevant parameters are essentially related to effect of spectral attenuation, length of the fiber optic run, bend radii, excitation and emission wavelengths, anticipated signal strength, and cost limitations.

Light attenuation in the fiber is significantly lower for silica cladding than for plastic cladding at wavelengths shorter than about 350 nm. The weaker the signal and the longer the length of the fiber optic, the more significant is this consideration, especially for short wavelength operation. For example, the 100-meter long probe required by the WES work at Savannah River led them to choose silica clad fiber. Based on the success of the NDSU group with 20-meter probes and 260 nm excitation, the attenuation for plastic-clad fiber for the 337 nm excitation wavelength of the nitrogen laser may be low enough that it could have been used instead. (The attenuation over 20 meters of fiber at 260 nm is comparable to that over 100 meters at 337 nm.) However, it is doubtful that there is sufficient transmission over 100 meters at 260 nm to obtain useful signals.

Bending losses are another factor to be considered. Generally, bending losses are higher for large diameter fiber and low numerical aperture fiber. Plastic-clad silica is not intrinsically worse than silica clad silica in this regard and is actually better owing to its higher numerical aperture. The transmission losses are highly sensitive to launching conditions. Underfilling the fiber considerably reduces the extent of microbending losses. Further details on the effect of fiber bend can be found in Reference 6.

Cost is important because the silica clad fiber is several times more expensive per unit length than is the plastic clad fiber. The 200 meters of fiber in the WES probes (100 meters

each for delivery and collection) represents an acquisition cost of about \$3000. If six collection fibers were used, the cost for fiber alone soars to about \$10,000. Whether the improvement in data quality afforded by more collection fibers is significant again depends on the specific details of a given experiment.

3. Detection System

The ideal detection system would provide simultaneous acquisition of the entire emission spectrum over the entire time scale of the emission. Such an ideal detection system doesn't exist. The OMA detector used by WES gives the entire emission spectrum, either integrated over time (non-gated mode) or in a selected time interval (gated mode). To obtain the entire time profile, it is necessary to advance the gate delay sequentially in a series of experiments.

In a sense, the NDSU approach is just the opposite. The monochromator/photo-multiplier tube/digital oscilloscope combination gives the entire time profile at a single emission wavelength. Repeating these measurements for a series of emission wavelengths (to generate a wavelength-time matrix) ultimately provides the same data as in the gated mode WES approach.

4. Data Analysis

Data analysis is still in a primitive stage. WES's approach is somewhat difficult to gauge since they have not provided too many details to date. Their basic philosophy in data analysis appears to concentrate on the emission intensity at 450 nm, the peak of the emission spectra for Diesel Fuel Marine. For sites where the contaminant is not known, the LIF signal is expressed in "equivalents" of DFM.**

** Personal communication between R. Olden of WES and J. Shinn of ARA, January 1993.

One way to improve the chemical specificity is to acquire additional data when a LIF response is encountered. For example, stop the push and vary the gate delay to acquire lifetime information. The AFSCAPS project used this approach of acquiring a WTM by stopping the cone whenever a higher count is obtained (either in the middle or at the end of a push) and acquiring the necessary data.

G. INFLUENCE OF FUEL TYPE AND SOIL MATRIX

Most LIF studies to date for environmental analysis have mainly dealt with aqueous media (e.g., Gillispie and Germain, 1992 [7]). Environmental uncertainties for ground water measurements arise if (1) multicomponent fluorescent compounds exist in solution, (2) turbidity (suspended solids content) is high, thereby decreasing the effective excitation energy due to scattering (producing a lower measured intensity), or (3) dissolved oxygen levels are variable leading to quenching of the fluorescence. Corrections for these effects may be made, depending on the development of LIF signal processing and analysis techniques or synergistic sensor technologies.

The NOSC group (8), in collaboration with WES, has shown that LIF results for soils are dependent on a larger and more complex set of variables compared to LIF measurements of aqueous solutions. Generally, the sensitivity appears to depend on soil type (e.g., surface area, grain size, mineralogy, and degree of soil aggregation), porosity, moisture content, saturation level and LIF response of natural fluorophores (e.g., humic acid). The presence of solids increases the amount of backscattering and decreases the effective penetration depth of the excitation energy. The following paragraphs summarize the main conclusions of the NOSC group study.

For both clay and sand matrices the fluorescence signal is determined only by the contaminant on or between the first grain layer, i.e., The grains in contact with the window. Although they could visually observe fluorescence penetrating slightly deeper into the sample, its contribution to the signal received at the detector is apparently negligible.

The observed fluorescence signal depends on the type of soil matrix. The fluorescence of DFM on Fischer sea sand increases rapidly with increasing DFM concentration. The signal versus concentration curve has a much lower slope for clay matrices such as attapulgite and bentonite. For example, at a fixed concentration of 50,000 ppm DFM the fluorescence signal is an order-of-magnitude greater for sand than for attapulgite clay. The attapulgite signal, in turn, is many times greater than for bentonite. It is clearly important that soil type be considered when analyzing LIF-CPT signals.

The possibility that the differential fluorescence response could be explained in terms of grain size and/or specific surface area was investigated by the NOSC group, but no clear conclusions emerged. Some success was obtained in correlating fluorescence response with an "available" surface area as opposed to the "specific" surface area. The authors concluded that the "fluorescent response of the fluorophore on sands and clays, though affected by several factors, is primarily controlled by the grain surface area available to the contaminant." Unfortunately, there does not appear to be a simple way to determine the "available surface area" apart from very extensive fluorescence calibration measurements.

The influence of water content on the fluorescence signal depends on whether the water is added to the soil matrix before the fuel or after the fuel has been added. The order effect is small for Fischer sea sand, but large for illite. In fact, the fluorescence of DFM on illite is much higher if water is introduced to the sample and then the DFM is added than for the reverse order. One must question whether the mechanism of mixing the samples is sufficient to bring them to equilibrium. The authors mention that longer term experiments are in progress. They also note "we have no reliable method to make continuous in situ moisture content measurements in soils to correct for this effect. Optical methods, based upon either the Raman peak of water or IR absorption and electrical methods based on soil resistivity are currently being investigated" (Reference 9).

SECTION III

LIF-CPT SYSTEM SPECIFICATIONS

A. INTRODUCTION

Presented within this section is a discussion of the basic LIF-CPT system, including the laser source, dye lasers, detection scheme, CPT LIF probe and computer control. A detailed list of components used to construct the system is contained in the appendix.

The basic laser system components are the following: a Nd:YAG pump laser, two separate and independent dye lasers, frequency doubling crystals to convert the visible dye laser output to ultraviolet, fiber optic probe, monochromator for wavelength resolution of the return fluorescence, photomultiplier tube to convert photons into electrical signal, digital oscilloscope for waveform capture, and control computer. The fiber optic probe for the cone penetrometer consists of a delivery and collection fiber, protective sheath, fiber optic mount within the cone, and sapphire window. The up-hole portion of the system is adaptable to either groundwater monitoring fiber-optic probes or an optical cone penetrometer probe.

Figure 2 is a schematic of the main system components: (1) a breadboard with laser and optical mounts and power supply generating signal for the delivery fiber, (2) the fiber optic probe, and (3) collection fiber fixed to a monochromator with photomultiplier tube (PMT), digital oscilloscope detection system and control computer (PC). The arrangement of the dye laser components on a 2-foot x 4-foot optical breadboard is shown schematically in Figure 3.

B. LASER SYSTEM

1. Nd:YAG Pump Laser

The tunable dye lasers are pumped by a Quanta-Ray GCR-12 Nd:YAG laser equipped with a harmonic generator accessory to provide second, third, and fourth harmonics at 532, 355, and 266 nm, respectively. The GCR-12 is an oscillator only model that provides a

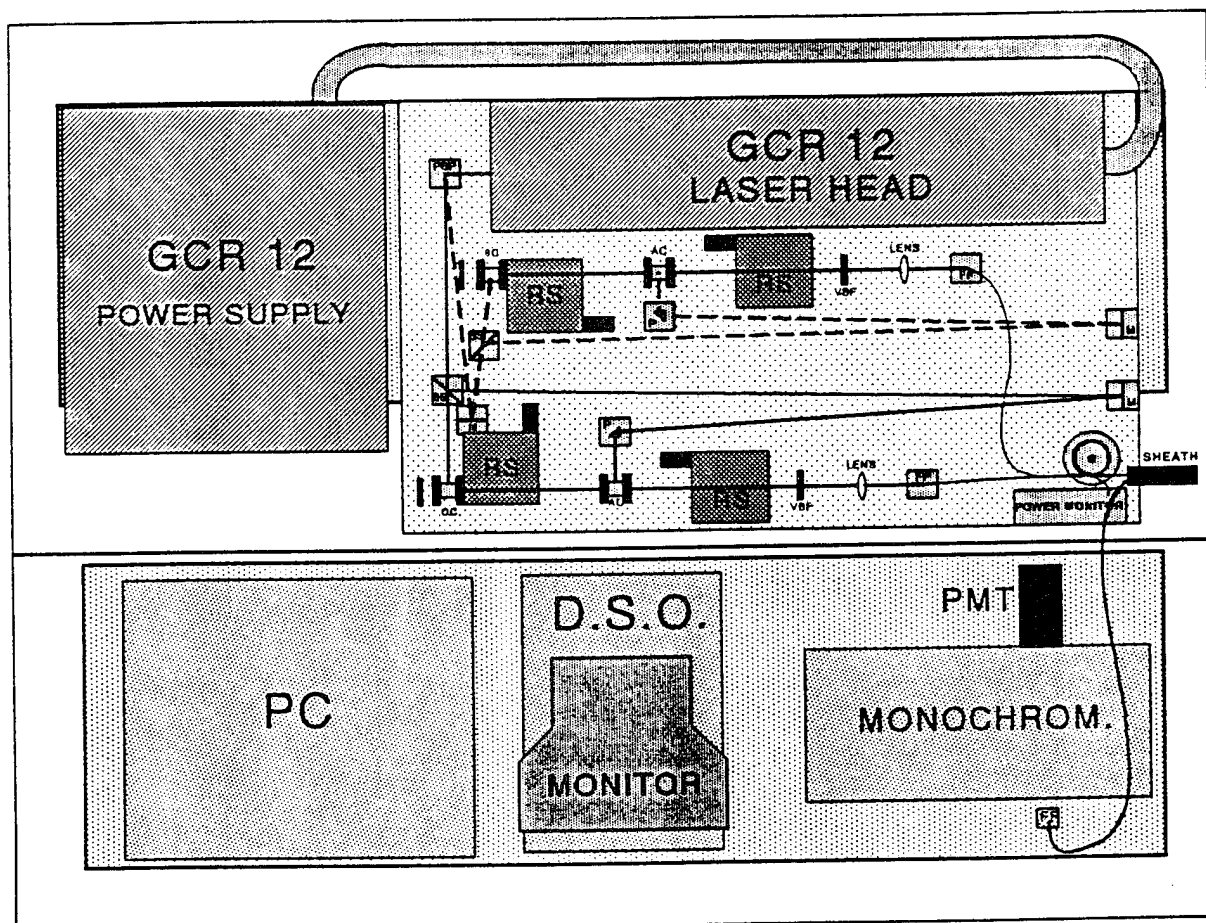


Figure 2. Schematic of Laser System.

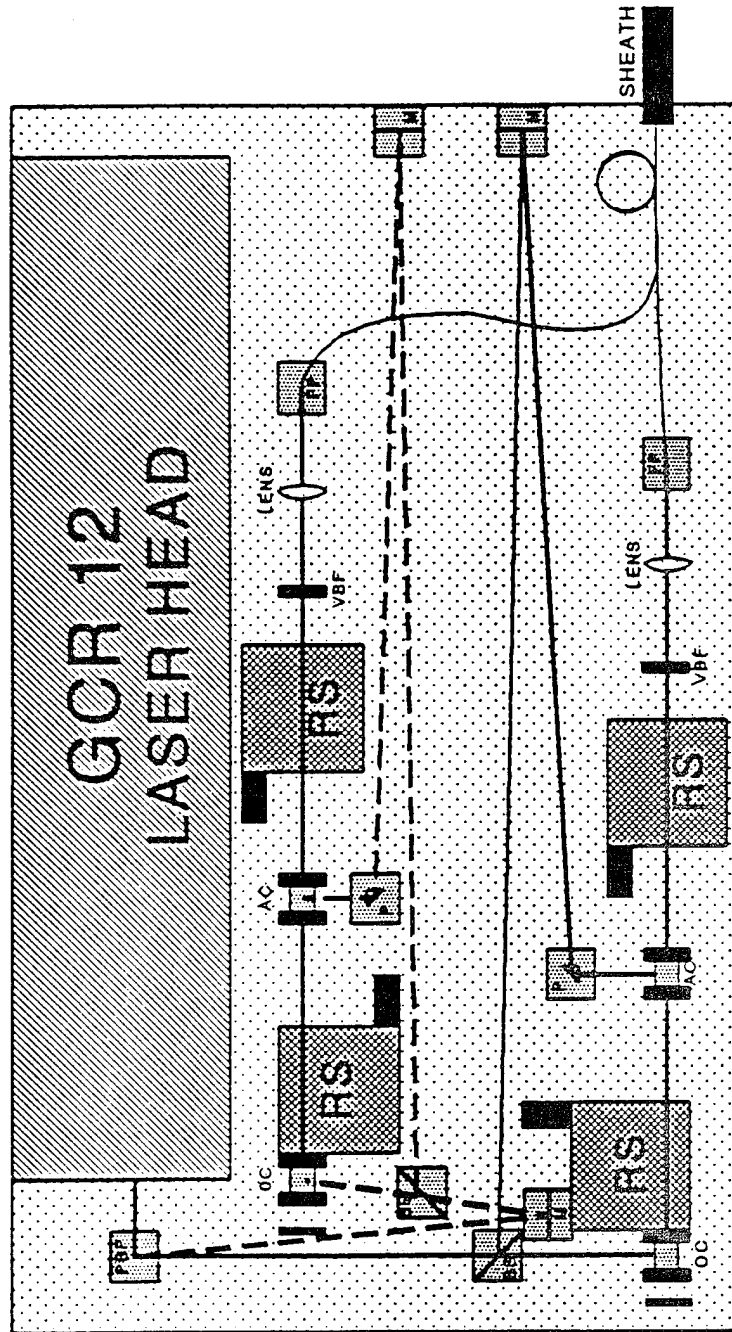


Figure 3. Schematic of Dye Laser.

near-Gaussian output beam approximately 1/4-inch in diameter. Pulse energies > 150 mJ at 532 nm and > 60 mJ at 355 nm are available at repetition rates up to 16 Hz, although pulse energy drops off above 10 Hz. Water cooling is provided by the laser power pack. Power requirements are 190-250 V, 10 amps, single phase. No external source of cooling water is necessary.

2. Dye Lasers

Fuel contaminants of concern during the Tinker AFB demonstration are JP-4, JP-5, and heating oil. Based on preliminary spectroscopic examination of these fuels in water and on soil provided from Tinker, it was determined that the optimal wavelength to use during a continuous push is approximately 285 nm. Photons of this wavelength were shown to give the strongest fluorescence signal, which was attributed to the emission of naphthalene and its methyl derivatives. Fluorescence of BTEX (benzene, toluene, ethylbenzene, and xylenes) requires shorter wavelength excitation, < 275 nm. The 266 nm 4th harmonic of YAG provides suitable excitation for all the BTEX components and naphthalenes, except benzene. Benzene requires wavelengths shorter than about 260 nm. On the other hand, compounds such as phenols and humic acids can also be excited at 266 nm. It is currently believed that the capability to vary the excitation wavelength will be required for fuel type identification.

Dye laser technology allows one to convert the fixed wavelength light from the Nd:YAG into a wavelength-selectable range. Ideally one would hope to directly generate tunable ultraviolet light by direct pumping of some UV dye, but this is not possible. It is necessary to first generate visible light that can then be frequency doubled into the ultraviolet. The following design considerations should be noted. The output of a dye laser typically begins about 30 nm or longer than the wavelength of the pump laser. Thus, with 532 nm pumping of Rhodamine 6G dye, the shortest wavelength readily achievable is about 560 nm, which is converted to > 280 nm by frequency doubling.

All work on this project was performed with 285 nm excitation, which is optimal for the jet fuels of primary interest to the Air Force. Development and evaluation of the 260 nm excitation source is planned for future projects.

High-performance dye lasers generally employ two or more stages, each with its own dye cell. Tunable radiation (the "lasing") is generated in the oscillator, which consists of flowing dye cell, cavity mirrors, and some type of wavelength dispersing element (grating or prism). The monochromatic light from the oscillator is input successively to amplifier stages, which increase the output power without further wavelength modification. The pump power (i.e., from the YAG) is distributed, usually in non-equal fashion, between the oscillator and amplifier stages. Typically about 20 percent of the pump light is directed into the oscillator cell with the other 80 percent incident on the amplifier cell after a spatial excursion of approximately 1 meter to delay its arrival at the amplifier cell.

The laser built for Tinker AFB uses Bethune prism dye cells of the style shown in Figure 4. Bethune cells use total internal reflection to create highly uniform illumination of a circular cross-section of dye passing through a small diameter bore drilled parallel to the vertex of a right angle prism. This design has been used occasionally, mostly for amplifier stages in ultrafast (subpicosecond) systems. Bethune cells are available as options for Lumonics dye lasers. NDSU found that Bethune cells offer very significant advantages for field laser purposes. The most significant advantage is that the pump light entering a Bethune cell does not require focussing. In fact, it must be collimated, or nearly-so, to maintain a total internal reflection condition in the cell.

3. Frequency Doubling and Fundamental Rejection

The output from the amplifier cell is frequency-doubled in an angle-tuned potassium dideuterium phosphate (KDP). Power levels are sufficiently high enough that no focussing is necessary. The fundamental is rejected with a colored glass filter and then the UV light is focused on the end of the fiber optic probe. A gentle input focus greatly minimizes potential problems of excitation fiber optic damage or generation of extraneous light in the fiber by nonlinear processes.

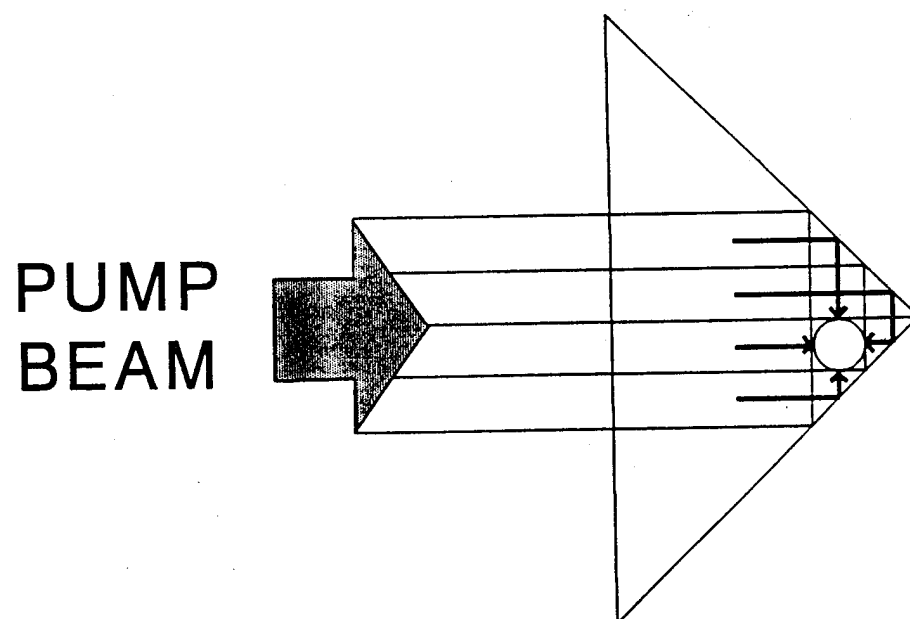


Figure 4. Schematic of Prism Dye Cell.

4. Detection System

Many monochromators in the 150-500 mm focal length range are commercially available. An important design issue is that of photomultiplier tube-digital oscilloscope versus CCD camera signal processing. The former gives full intensity versus time information, albeit at a single emission wavelength. The latter gives full intensity versus emission wavelength information, albeit at a single time slice (or integrated over all time). If one has the option to collect data for a minute or more, either device can add the missing information. For example, in the digital scope-PMT approach, one can acquire waveforms for several different emission wavelengths to generate a wavelength-time matrix (WTM). In the WES approach, one could advance the gate of their OMA to fill out the full time profile.

The field laser system was designed with a view toward future possible applications, including incorporation of a CCD camera. It was desired to maintain the option of quick switching between CCD and PMT-scope detection, or even, better, simultaneous operation. At this stage, the two best monochromator options are Chromex® 500-IS and the Spex 270-M. Both contain toroidal mirrors, which minimize cross-talk for separate fiber inputs (not done here, but likely option in the future). The Chromex® 500-IS has a flipping mirror to switch between two output ports, one that could be a PMT (operation as spectrometer) and one that could be a CCD (operation as spectrograph). However, simultaneous operation is not possible and switching would take several minutes and require realignment. The Spex 270-M appears to offer more flexibility and is completely interfaceable with communication over the RS-232 serial interface. In this fashion, one can set wavelength and slit width via computer control. Diagnostic and calibration routines are built into the 270-M.

The wavelength-resolved fluorescence passed by the monochromator is converted to an electrical signal with a photomultiplier tube (EMI-9813). The PMT signal is directed to a Tektronix model 2440 digital oscilloscope for signal averaging. The temporal width of the frequency-doubled laser pulses is 5-7 ns and the pulse repetition rate is 10-15 Hz. The digital oscilloscope samples each decay curve at 500 megasamples/sec, i.e., a point on the waveform is acquired every 2 ns. If the fluorescence signal is strong and the molecular lifetime long, the

fluorescence temporal profile can be generated from a single laser excitation pulse. More often multiple laser shots are acquired, either to improve signal-to-noise for trace analysis or to yield enough data points to adequately define the decay curve. For time bases shorter than 50 ns/division, the oscilloscope automatically goes into an equivalent-time sampling mode to provide 50 sampling intervals per division. Typical time bases are 10 or 20 ns/div, which results in 0.2 or 0.4 ns sampling intervals, sufficient to determine lifetimes down to 1 ns.

On an individual trigger the scope provides 8 bits of vertical resolution for a maximum of 255 counts per channel, far less than the 10,000 or more counts per channel typical for lifetimes determined by time-correlated single photon counting. Signal averaging increases the effective number of bits.

5. Control Computer

The entire system is under the control of a personal computer. Stepper motors drive the tuning mirror of the dye laser oscillator, the rotation stage on which the doubling crystal is mounted, and the leadscrew of the emission monochromator. Computer control also sets the high voltage on the PMT and provides communication with the digital oscilloscope via a GPIB bus.

C. PROBE DESIGN

The LIF-CPT probe is designed to measure tip and sleeve stress, pore pressure and LIF simultaneously. The fiber optic cable connected to the laser spectrometer, and six-pair electrical conductor connected to the CPT data acquisition system, are routed through the interior of the push tubes to the CPT probe. Two load cells measure vertical resistance beneath the tip and frictional resistance on the side of the probe, respectively. The pressure gauge located above the cone tip monitors the pore water pressure. A more complete description of the CPT and test method is given in Volume II.

The fiber-optic LIF sensor essentially consists of the fiber-optic cabling, positional mount and sapphire window. The sensor design employed for this project is a modification of ARA's existing CPT probe and NDSU's fiber optic probe for ground water monitoring. WES's two-fiber design was considered, but was not suitable for the NDSU seven-fiber configuration. A LIF probe was designed for the NDSU seven-fiber bundle as discussed below.

The 6-around-1 fiber optic configuration using 600-micron plastic-clad silica core fibers was used for the fiber optic cable. The Tinker AFB demonstration required relatively shallow pushes so that a 30-meter instrumentation cable was satisfactory. From experience with groundwater monitoring fiber optic probes, this is short enough for use of plastic-clad silica (PCS) fiber, as opposed to the silica-clad silica (SCS) fiber used by WES. The 30-meter length was estimated to allow penetration depths of about 15 meters (45 feet), with excess cable required for hook-up above ground and for storage of the push tubes (1-foot separation).

The LIF-CPT fiber optics were fabricated using Fiberguide SPC600N fibers. The fiber has a 600-micrometer diameter silica core, 700-micrometer diameter plastic cladding, and 800-micrometer diameter nylon jacket. The seven fibers packed as tightly as possible would fit within a cross-sectional area of under 2 mm diameter. For protection of the fibers within the instrumentation cable, they were passed through a 1/4-inch O.D., 3/16-inch I.D. Teflon tube.

A 7-fiber, 600-micron core, PCS cable costs \$23.80/meter versus \$119.00/meter for a similar SCS cable arrangement. As discussed in Section II, the transmission properties of SCS fiber for wavelengths less than 350 nm are significantly greater than PCS fiber. Therefore, a less expensive SCS fiber bundle consisting of smaller-diameter fibers and/or fewer collection fibers could deliver equivalent light, as well as having significantly smaller bending losses. NDSU's laser launching does not use the full-fiber aperture and consequently takes advantage of a larger-diameter fiber without invoking transmission losses due to bending (Section II). Also, usage of fewer fibers would require a more elaborate mounting system at the probe end of the cable, similar to the WES design. NDSU's 6-around-1 cable was chosen for the probe after assessing the potential bending losses in the laboratory.

At the probe end, the fibers were embedded into epoxy (Torr-Seal from Varian) and packed into a glass tube. The glass tube, in turn, is fixed into a fiber-optic positioner which is emplaced in the LIF sensor module. The central fiber optic serves as the delivery cable. The fiber optics are turned within a 1.25-inch I.D. cylindrical insert using a 0.25-inch tube with a 1.25-inch radius of curvature. This positions the fiber axes to be approximately perpendicular to the window. The fiber tip to window distance is approximately 0.12 inch (3 mm).

The 0.08-inch thick, 3/8-inch diameter sapphire window is set on the side of the cone approximately 1.75 feet above the tip of the CPT probe. Somewhat similar to the WES design, a 0.6-inch wide, 0.05-inch deep flat is milled for 2 inches below and 1 inch above the window on a line parallel to the cone axis. This brings the outside face of the window flush with the cone surface to ensure intimate contact to the soil with minimal smearing. A 0.187-inch port lies below the window, allowing a 0.09-inch shoulder for epoxying the window to the rod. Alternatively, a removable window design was made. This consisted of a threaded, 0.4-inch diameter steel cylinder with the same window mount described above.

Two LIF-CPT cable arrangements were used, one with ARA's standard 0.54-inch diameter grout tube and one without. The grout tube was to be used with a self-grouting module reserved for future designs. The grouting tube and fiber optic and electrical signal cables were wrapped with nylon fibers mesh. The wrapping appear to kink the fiber optic cable tube and make handling the rods more difficult than need be. The second cable system took advantage of the annulus made available by the removal of the grout tube. A half-inch diameter Carlon Carflex® conduit was used to protect the fiber optic and conductor cables. Threading these cables through the conduit was difficult, but the conduit was found to facilitate rod handling during pushes.

SECTION IV

LABORATORY TESTING PROGRAM

A. BACKGROUND

The laboratory test program was conducted to evaluate the sensitivity of the LIF-CPT system to fuel contaminated soils typical of the field demonstration sites at Tinker AFB. As shown during the technical review, several key issues, including system accuracy, precision, specificity, and detection limits, had either not been addressed in the open literature or by either the NOSC or WES groups. For example, results from NOSC and WES are typically presented in terms of a "DFM fluorescence equivalent," which is the laboratory concentration of Diesel Fuel Marine (DFM) that yields the same signal as observed in field data. However, for many of the sites previously investigated, the primary contaminant is not DFM and the concentration of the actual contaminant is not known.

Studies (Reference 8) have shown that the fluorescence response of a given fuel is influenced by soil type and soil moisture level. However, their data were taken in the absence of the soil compression characteristic of actual cone pushes, the role of such compression being unknown. Another factor that could degrade accuracy and precision is variable light loss in the fiber caused by bending.

The laboratory testing program was formulated and conducted to address these issues. Specific objectives of the program included evaluating:

1. Instrument uncertainties associated with using fiber optics in cone penetrometer testing, particularly transmission loss due to fiber bending and effect of fiber geometry at the sapphire window.
2. Spectral characteristics of neat fuels in the aqueous phase and fuels in soils typical of Tinker AFB;
3. Influence of soil moisture for representative Tinker AFB soil samples;
4. Influence of soil compression and it's influence on fluorescence properties;
5. For a given fuel type, the relationship between contaminant concentration and fluorescence intensity.

Details of the laboratory program, which was conducted jointly by ARA and NDSU, are contained in Volume IV, Appendix K, entitled "Laboratory Validation Test Plan."

B. SECTION ORGANIZATION

The laboratory testing presented in this section consisted of three major efforts; (1) selecting and characterizing representative soils from Tinker, (2) evaluating the effect of bending on the LIF signal, and (3) determining the sensitivity of the LIF system to expected fuel contaminants. Characterization of representative soils from Tinker AFB was conducted jointly by ARA and NDSU. Testing included determination of the soil type, grain size distribution, soil components and index properties, and are presented in Subsection C. An important consideration which was raised as a part of the technical evaluation was the effect of bending on the LIF signal and the optimal location of the LIF fibers relative to the sapphire window. To evaluate this effect, tests were conducted at NDSU and are summarized in Subsection D.

Determination of the optimum LIF excitation wavelength and the relative difference between contaminated ground water and soils was conducted by the NDSU group and is presented in Subsection E. This section also includes a discussion of the major fuel components that are expected to provide the strongest fluorescence signal and the effect of humic acids, which are naturally occurring materials that are known to fluoresce strongly.

Within each subsection a description of the experimental methods is presented, followed by a discussion of the testing performed and the test results. A summary of the laboratory testing results is contained in Subsection F.

C. SOILS SELECTION AND EVALUATION

Soils samples used in the laboratory testing were obtained from the North Tank Area (NTA) at Tinker AFB, Oklahoma. Samples were collected in late May, 1992 and containerized and sealed in four 5-gallon buckets. The NTA soil was taken from stockpiles of soil excavated from above the 50-foot diameter underground fuel oil storage tank; no non-native fill components or fuel contamination was observed in the samples.

Visual and physical analyses of the NTA soil were performed by ARA and the NDSU Testing Laboratories. Testing by ARA included grain size distribution using sieve and hydrometer analyses, Atterberg limits, soil grain specific gravity, and water content. The grain size distribution and Atterberg limits are used for soil classification purposes. As provided in the test plan, a phase-relationship spreadsheet has been developed to calculate the soil moisture and percent saturation for different compaction states. NDSU conducted mineralogical analyses of the sand, silt, and clay fractions at the solids Testing Laboratory at NDSU. The mineralogy was obtained using standard X-ray diffraction methods. Loss on ignition for total organic content was determined as well.

The soil studied was heterogeneous in texture and color, with aggregates or lumps of fine sand that were somewhat indurated, but could be crushed in fingers. This material was red in color according to the Munsell soil color chips. It was visually estimated that the "sandstone" lumps made up approximately 5 percent of the total soil sample. Aggregates of very dark gray loamy material were present and composed approximately 5 percent of the soil. The majority of the soil was a sandy loam and was weak red in color. This component of the soil was generally granular and made up approximately 85 percent of the sample. Pebbles, organic matter in the form of roots and miscellaneous trace materials compose the remaining 5 percent.

The NDSU Soils Department and ARA did a quantitative analysis of the soil texture using sieve and hydrometer methods. The results of that analysis are listed below.

1. Sand: 0.3 percent Very Coarse Sand (1 to 2 millimeters)
0.8 percent Coarse Sand (1000 to 500 micrometers)
1.8 percent Medium Sand (500 to 250 micrometers)
46.4 percent Fine Sand (250-100 micrometers)
16.2 percent Very Fine Sand (100 to 50 micrometers)
Total Sand Component = 65.5 percent

2. Silt: 10.5 percent Coarse Silt (50 to 20 micrometers)
7.9 percent Fine Silt (2 to 20 micrometers)
Total Silt Component = 18.4 percent

3. Clay: Total Clay Component = 16.1 percent

Sand grain shapes were rounded to angular. This detail can be interpreted to mean that the grains have undergone significant transport and reworking. The water content of the soil sample was determined to be 15 percent. The organic matter made up approximately 1 percent of the sample by weight according to a loss on ignition test.

4. Mineralogy: The individual grain separations were retained for qualitative powder X-ray diffraction analysis. The clay-sized component of the soil contained the clay minerals kaolinite, illite, and smectite. Quartz, plagioclase, and potassium feldspar were present as minor mineral components. A separation containing silt and clay-sized grains had a mineralogy the same as the clay fraction, but contained more quartz. Quartz made up essentially all of the crystalline phases present in the fine and very fine sands. Since these were the most abundant grain sizes, quartz was deemed the predominant mineral in the soil. Larger sand grains were examined visually under a binocular microscope and appeared to be mostly quartz. Other grains identified visually in the very coarse, coarse, and medium sand components were iron oxides, feldspars, and lithic clasts.

5. Geotechnical: The soil grain-size distribution indicates that the NTA soil is a sandy clay. Using the Unified Soil Classification system, the soil is classified as a clayey sand of low plasticity. The Liquid Limit was 26, the Plastic Limit 18, and the Plasticity Index 8. The specific density was determined to be 2.68 and is consistent with the predominant quartz mineralogy.

D. FIBER OPTIC BENDING LOSSES AND POSITIONING

1. Bending Losses

Although past experience by the NDSU group has not revealed any apparent bending loss problems, this issue was briefly investigated. A 20-meter long, 6-around-1, probe was used to measure the fluorescence of 0.001 M naphthalene in water with 260 nm excitation and

334 nm emission wavelengths. Intensity versus time waveforms were taken with the fiber probe uncoiled (i.e., with loose bends), with three one-inch radius bends placed approximately midway along the length of the probe, with six such one-inch bends, and then after removal of those bends. For each condition the waveform was acquired by averaging over 256 laser shots.

Further evidence on bending losses comes from a recent journal article by Boechat (Reference 6), wherein the propagation of light from the Nd:YAG fundamental at 1064 nm was monitored and modelled. The calculations were reproduced and then repeated for short wavelength excitation conditions. The susceptibility to bending loss is even lower at the shorter wavelengths. Another favorable feature is that fiber launching in the NDSU system employs a very gradual focus, which helps to minimize losses.

The results of the bending study are shown in Figure 5. The vertical and horizontal scales are 50 m/division and 20 ns/division, respectively. There is no effect of bending evident in the data. The variations in the intensities are consistent with the usual degree of signal reproducibility. Past experimentation had shown that even with under 0.5 inch radius of curvature, it is necessary to apply very great pressure (for example, by clamping the fiber between two small diameter metal rods) in order to cause light leakage between the cladding and the buffer. It might be noted here that fiber optics are most susceptible to light leakage of this type in the first meter or so after launching with different modes showing different degrees of light leakage. The most sensitive modes are lost first. While bending had little effect on light losses, the sharp bend angle in the LIF-CPT probe had a significant effect on maintaining focus of the light beam, as discussed in Section V.

2. Effect of Fiber Position

The effect of varying position of the fiber optic probe relative to the sapphire window was examined with the soil mold described in Volume IV, Appendix K. A sample of 1 percent JP-4 in Tinker soil (10 percent water content) was prepared, placed in the soil mold, and lightly compressed. The soil mold was positioned so that one of its three sapphire windows was facing up. The fiber optic probe was located at various positions ranging from flush with the outside

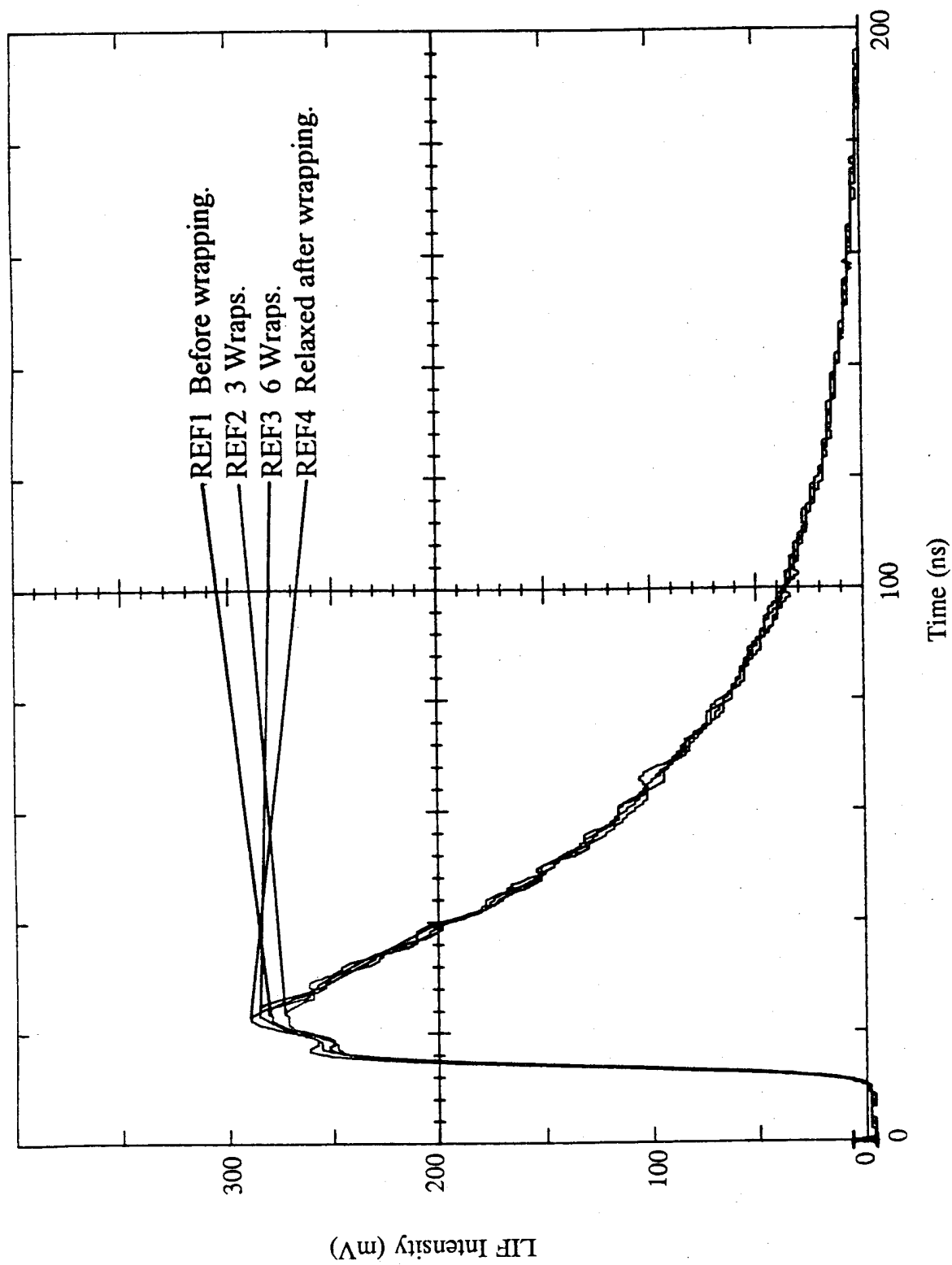


Figure 5. Effect of Bending 600 Micron Plastic Clad Fiber Optic Around a 1-Inch Diameter Steel Mandrel.

of the sapphire window up to 10 mm away. The fluorescence signal at 334 nm was measured and recorded.

Results from the distance dependence study are shown in Figure 6. One might expect the maximum signal intensity to be realized with the probe flush against the window, but this is not the case because the fibers can only collect light within a certain cone. When the probe is too close to the sample, some of the emission is "screened" from the collection fibers. On the other hand, as the probe is moved away from the window, the solid angle of the isotropic emission intercepted by the collection fibers is reduced. Competition between these two factors leads to the existence of a maximum in the curve. The maximum fluorescence is achieved at about 1.5 mm from the window. In the LIF-CPT probe, space and clearance constraints forced a distance of no less than 3 mm, in which case about 50 percent of the maximum possible fluorescence signal is achieved.

E. FLUORESCENCE SPECTROSCOPIC CHARACTERIZATION

Fuels particular to the Tinker AFB demonstration sites: fresh JP-4 and JP-5 and recovered fuel oil No. 2 from the North Tank Area at Tinker contain aromatic hydrocarbons, such as BTEX compounds (Benzene, Toluene, Ethylbenzene, and Total Xylene) and polycyclic aromatic hydrocarbon (PAH) compounds (e.g., naphthalene, anthracene, phenanthrene). Optimal detection must use excitation wavelengths in the near ultraviolet (250-350 nm) range to excite these compounds. BTEX compounds tend to have maximum fluorescence intensity for excitation wavelengths near 266 nm, producing emission maxima near 290 nm. PAHs fluoresce over a broader range of UV excitation wavelengths and generally have a higher fluorescent response than the BTEX. Naphthalene, a component of the above fuels, has maximum emission intensity at 335 nm produced with a 280 nm excitation wavelength. NDSU's prior spectroscopic work on aqueous solutions of JP-4 fuel revealed that, using optimal settings for the excitation and emission wavelength, the PAH fluorescence is significantly larger than BTEX fluorescence. As these optimal wavelengths and the effect of soils on the spectral characteristics had not been determined, the laboratory program concentrated on evaluating these optimal wavelengths.

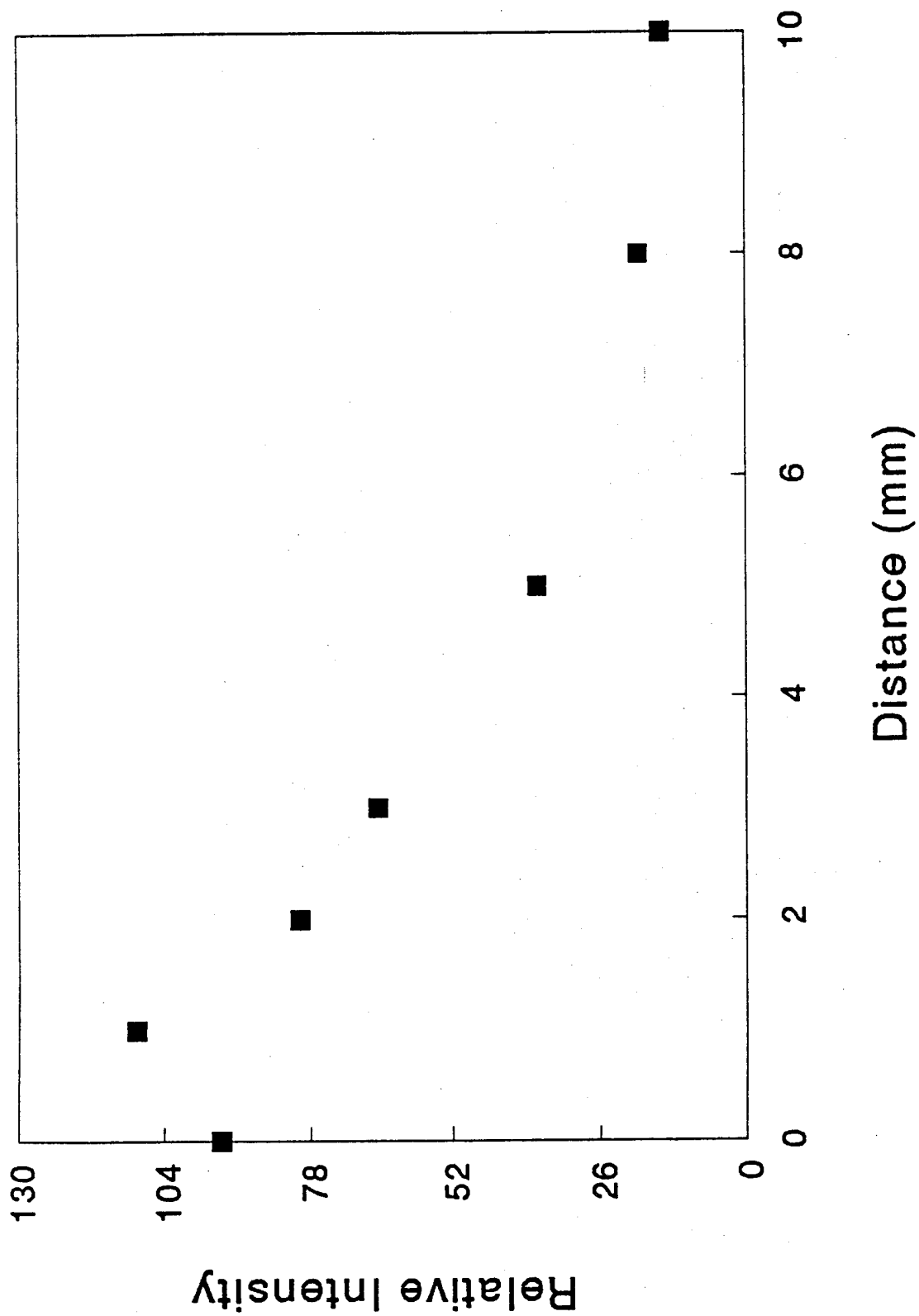


Figure 6. Plot of LIF Relative Intensity as a Function of Distance from Sapphire Window. Test Conducted Using 1 Percent JP-4 in Tinker Soils.

1. Testing Methods

Fluorescence and fluorescence excitation spectra of the fuels as neat liquids, as aqueous solutions and mixed with soil were measured with a Spex Model 2T2 Spectrofluorimeter. The Spex employs a xenon arc lamp source, double excitation and emission monochromators, and single photon counting detection. Using the fluorimeter, fluorescence intensity is reported in counts per second (CPS). Previous work^{***} at NDSU has demonstrated the spectrofluorimeter data are representative of that obtained with laser excitation and digital oscilloscope detection.

Lifetime measurements were performed with a system very similar, but not identical, to the field laser system. The excitation source was a GCR-11 Nd:YAG laser operating in fourth harmonic (266 nm) mode; tunable laser excitation was not used in the laboratory phase. The emission monochromator was a McPherson Model 218. The photomultiplier tube, digital oscilloscope, and control software were the same as in the field system. The fiber optic probe had a 10-meter long excitation fiber but only a 1-meter collection fiber.

A soil calibration chamber was designed to allow simulation of the stresses which occur as the CPT probe is inserted into the ground. Previous testing by the NOSC and WES groups had not addressed soil compression around the CPT probe. It was believed that in saturated soils the effect of increased pore pressure and reduced void space at the CPT/soil interface conditions could influence the LIF response. The chamber consists of a steel cylinder with steel pistons inserted at both ends. The lower piston has three sapphire windows and is stationary relative to the cylindrical sleeve. The upper piston compresses the soil in a uniaxial manner by screwing down on bolts connecting both the upper and lower piston base plates. The screw assembly is capable of transmitting uniaxial stresses of 2,000 psi. Both pistons have ports to allow interstitial fluid to pass to and from the soil chamber, with the lower port being sealed for this experiment. Filter paper is placed over the grooved piston head surfaces to prevent soil

^{***}Personal communication from Dr. G. Gillispie of NDSU to J. Shinn of ARA, January 1993.

from escaping through the ports as fluid is pumped into or out of the cell. Both pistons have O-ring seals to the cylinder.

Sapphire windows for the calibration chamber are 0.08-inch thick and have a 3/8-inch diameter. Each window is mounted within a 3/8-inch diameter inset above a 1/4-inch diameter port in the lower piston unit. The hydrostatic burst pressure for the window is 2,700 psi, but the presence of the 1/16-inch lip and the decrease in effective surface area should double that limit (see manufacturer's data charts). The uniaxial chamber allows soils to be pressed against the window with pressures similar to CPT push conditions. Details of the chamber are contained in Volume IV, Appendix K.

2. Preparation of Neat Fuels, Aqueous Solutions and Soil Samples

Neat fuels and aqueous solutions were held in standard fused-silica 10 mm x 10 mm cuvettes. The aqueous solutions were prepared by stirring 1 mL of fuel with 100 mL of charcoal filtered distilled water for several hours. The beaker containing the fuel water mixture was covered with a watch glass during the mixing in order to minimize loss of volatiles. It was observed that not all fuel components dissolved in water with the 1 percent (volume/volume) loading. The nondissolved phase is predominantly comprised of less volatile aliphatic hydrocarbons, and the spectral properties of these compounds are not addressed in this study.

Soil samples were prepared of processed and "as is" NTA soils. The processed soil were dried, lightly crushed and sieved, moistened to known levels via tumbling, loaded with a known amount of fuel, and then homogenized by further tumbling. The soils were dried in 100-gram batches by heating in a microwave oven. The sieving removed very little material, i.e., after the lumps in the dried soil were broken up, nearly all material passed through the No. 40 mesh (grain diameter < 0.025 inches) sieve.

One-hundred gram soil samples were measured and a predetermined quantity of charcoal-filtered distilled water was added to give the desired moisture content. The soil water mixture was loaded into either polyethylene or glass jars and tumbled for 2 hours. However,

after only a few minutes of tumbling the soil would ball-up into spherical form. Depending on the water content, as much as half the soil material was transformed into these spheroids, which sometimes attained radii of up to 3-4 mm. The balls were lightly crushed with a glass rod or stainless steel spatula and the tumbling resumed. Over a period of time the size distribution of the balls tended toward smaller radii.

After the soil was moistened to the desired level, a known amount of fuel was added to the soil samples in the same fashion with tumbling. Similarly, unprocessed soils were mixed or tumbled with fuel.

3. Discussion of Aqueous Solution Fluorescence Spectra

The first task undertaken was determination of the optimal excitation wavelength for the cone penetrometer pushes. Aqueous solutions of JP-4, JP-5, and the recovered NTA fuel oil were prepared and their fluorescence and excitation spectra acquired with the SPEX spectrofluorimeter. The excitation wavelengths of greatest relevance are 260, 266, 280, and 337 nm. The output wavelength of the Nd:YAG 4th harmonic is 266 nm and this is probably the logical choice for a non-tunable system. However, a limitation of a 266 nm source is that it is too short for excitation of benzene fluorescence, which requires excitation photons with wavelengths of 260 nm or less. Both 260 and 266 nm efficiently excite the BTEX components exclusive of benzene. These are also comparably good excitation wavelengths for the fluorescence of naphthalene and its 1- and 2-methyl derivatives. Switching the source wavelength to greater than 280 nm suppresses any BTEX emission, but the naphthalene signal should be maintained. Finally, 337 nm experiments allow one to make connection with the nitrogen laser experiments of WES; this longer wavelength is insufficient for BTEX or naphthalene fluorescence, but suffices for at least some of the larger PAHs such as phenanthrene or benzo-pyrene.

A comparison of the spectral signature of JP-4 and JP-5 at a 266 nm excitation is plotted in Figure 7. The data reveal strikingly similar fluorescence spectra. The normalized JP-5 spectrum shows slightly lower intensity for wave lengths less than 310 nm, but the agreement for wavelengths greater than 310 nm is good. It was hypothesized that naphthalene (or

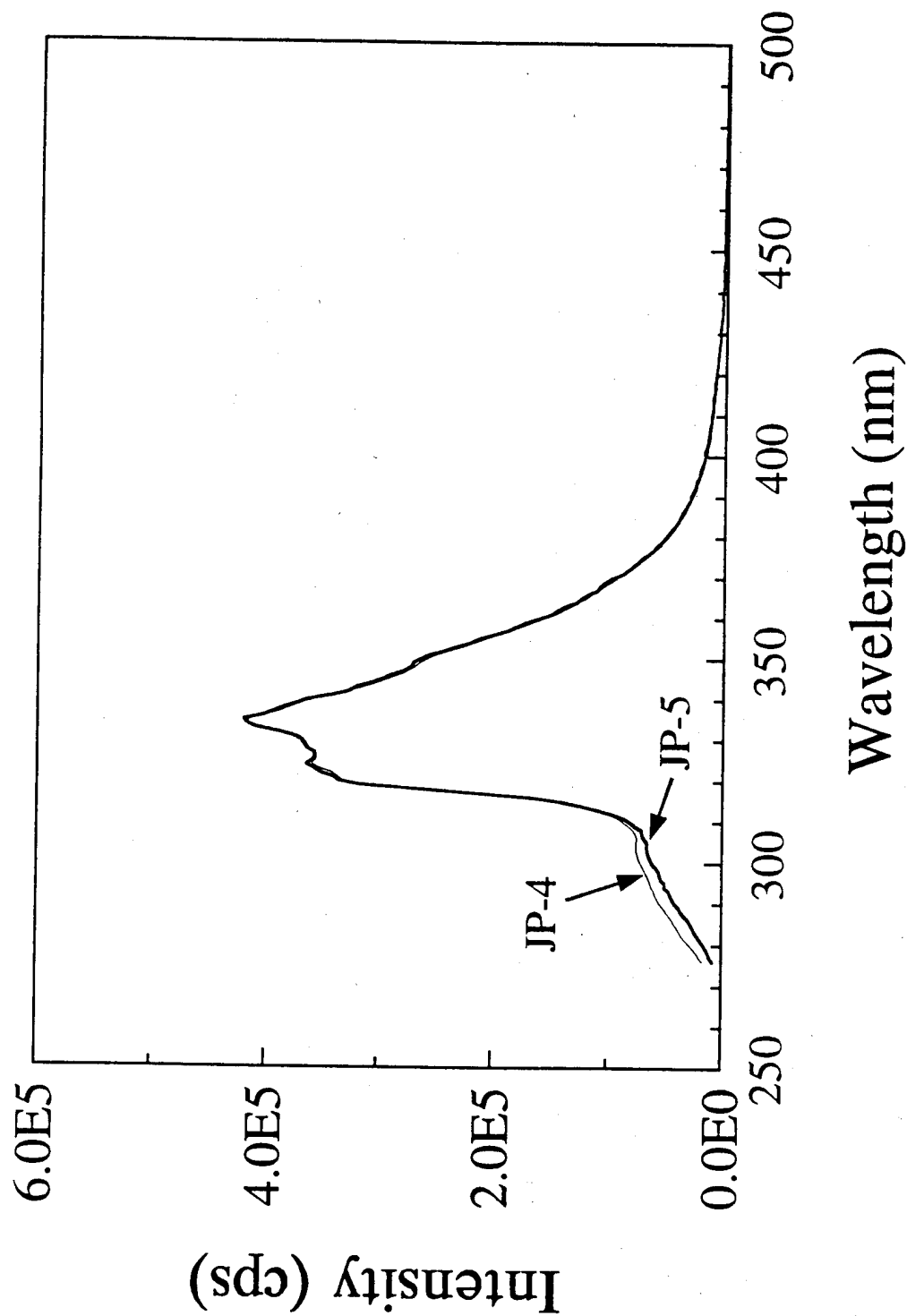


Figure 7. Comparison of JP-4 and JP-5 Spectra in Water. Excitation at 266 nm. BTEX Compounds Signal from 280 nm to 300 nm, with PAH's Primary Source of Fluorescence Above 300 nm.

naphthalene-like) molecules are the source of the longer wavelength emission. The hypothesis was tested by a comparison under identical excitation conditions (again 266 nm) of JP-4 and naphthalene aqueous solution fluorescence.

The agreement between the JP-4 and naphthalene spectra is not perfect (as shown in Figure 8), but the characteristics of the two spectra are quite similar. The JP-4 fluorescence is slightly wider than that for naphthalene, most noticeably on the trailing (long wavelength) end. Undoubtedly there are additional contributions from 1-methyl-naphthalene and 2-methyl-naphthalene, both known to have similar fluorescence properties to that of naphthalene.

There appears to be a good potential for fluorescence as a quantitative characterization tool. The JP-4 fluorescence at 270 nm to 310 nm is due to BTEX compounds. As expected, naphthalene is absent in fluorescence at these wavelengths.

Next, the excitation wavelength was shifted to 280 nm, which is too long to excite BTEX fluorescence, but still close to the absorbance maximum of naphthalene. The aqueous JP-4 spectra in Figure 9 show that the longer wavelength spectral distribution is nearly invariant to excitation. As expected, the short wavelength portion (due to the BTEX component) is lost upon longer wavelength excitation.

Fuel oil No. 2 recovered from the North Tank Area during remediation exhibits a strong naphthalene-like fluorescence as well, as shown in Figure 10. Note that the recovered oil fluorescence, normalized to the same maximum intensity as for naphthalene, shows greater fluorescence in the region above 400 nm. A contributing factor is emission from larger PAHs, similar to the interpretation the NOSC group. However, one must be aware of the contribution of humic acid fluorescence in this region also, as discussed in Subsection E.6.

4. Neat Fuel-Fluorescence Spectra

The spectra of neat JP-4 and JP-5, excited at 266 nm, are shown in Figure 11. The JP-5 emission spectrum, having less light volatile organic compounds than JP-4, shows a slightly

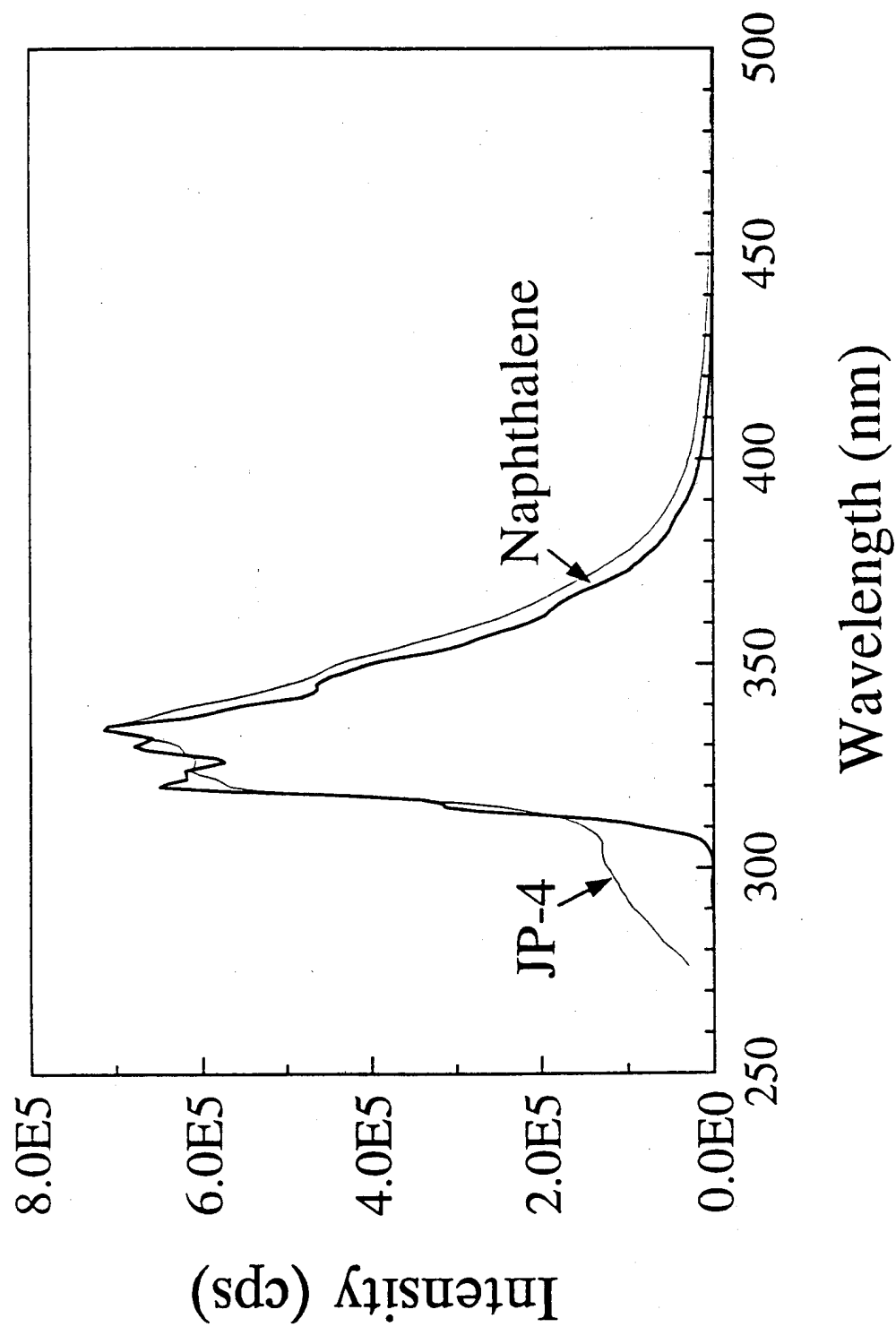


Figure 8. Comparison of JP-4 and Naphthalene Spectra in Water. Excitation Source of 266 nm.

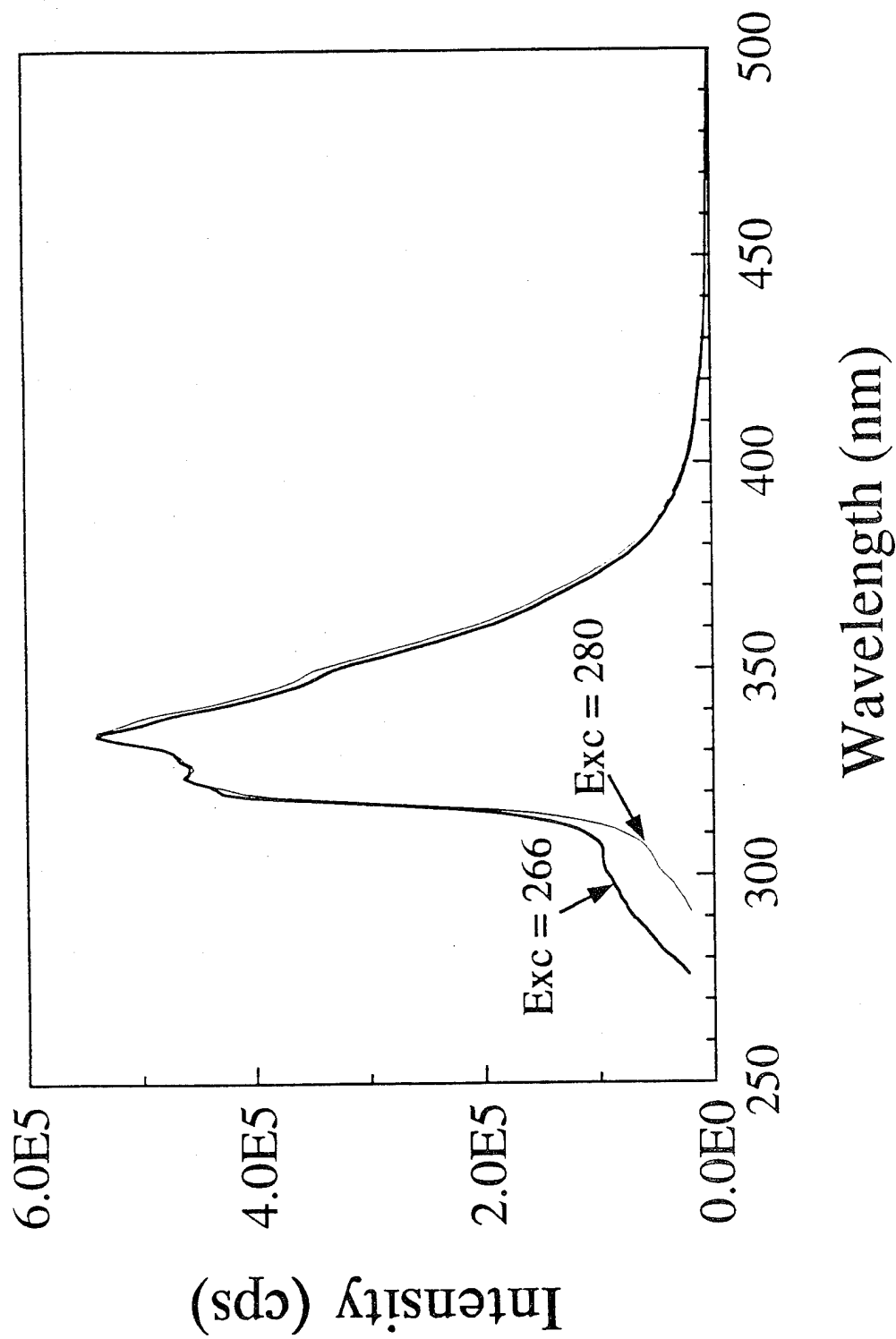


Figure 9. Comparison of Aqueous Solution of JP-4 Spectra, Excited at 266 and 280 nm. The BTEX Signature of the 280 nm Excited Sample is Greatly Reduced, Above 310 nm the PAH Signatures are Nearly Identical.

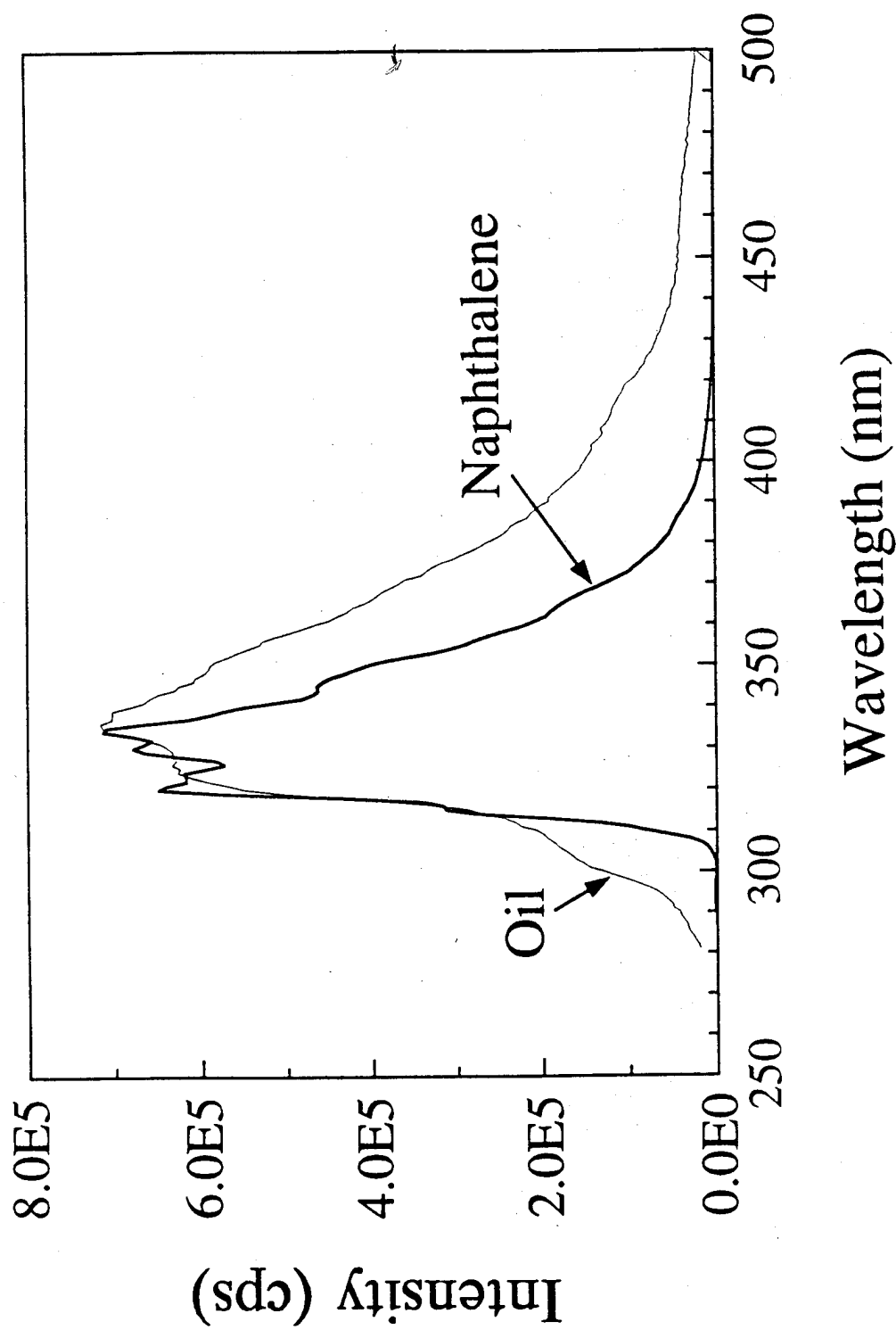


Figure 10. Comparison of North Tank Area Product Oil and Naphthalene Spectra. Increased NTA Oil Response at Wavelengths Greater Than 350 nm Due to Larger PAH Compounds Found in Heating Oil.

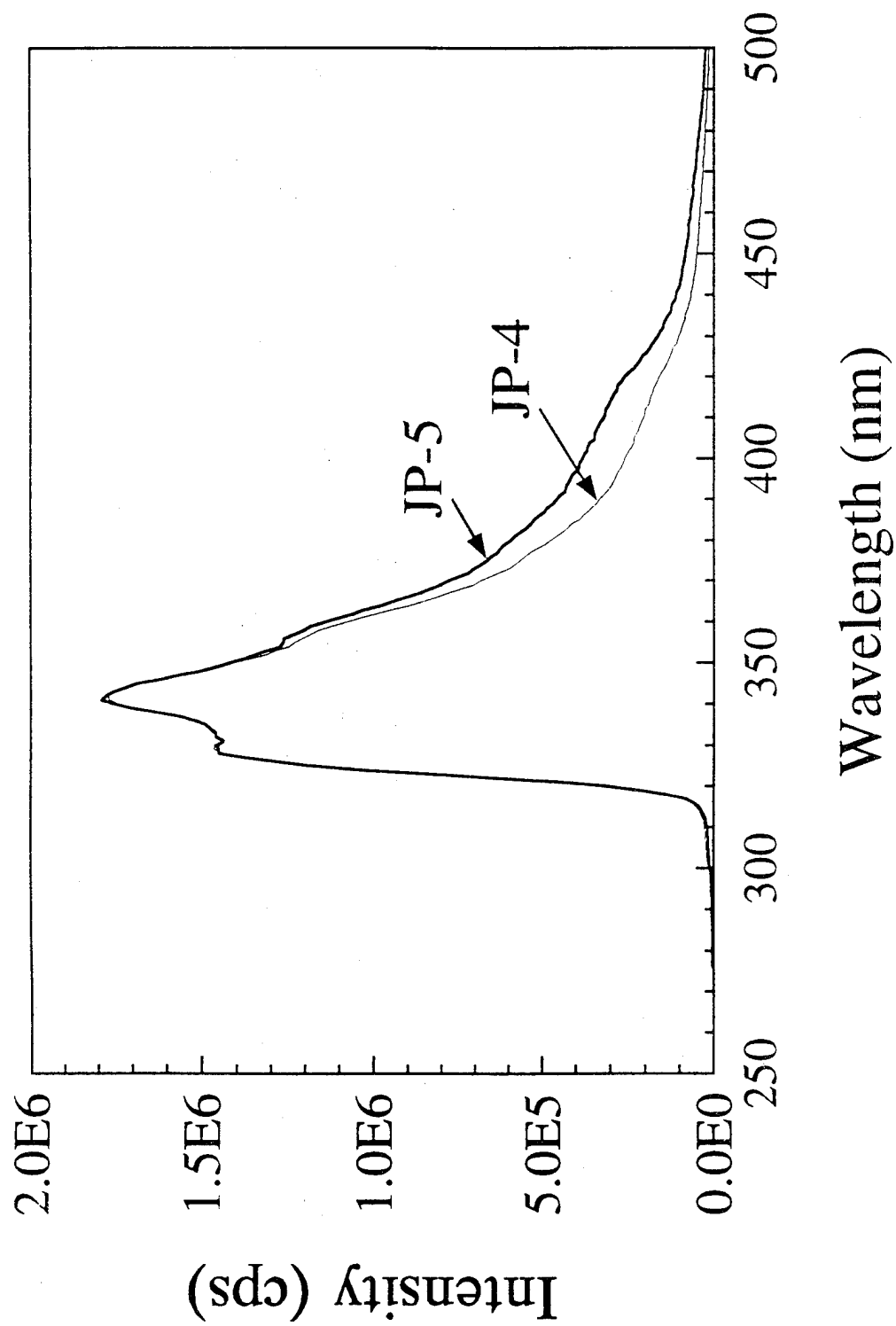


Figure 11. Comparison of JP-4 and JP-5 Spectra. Increased JP-5 Emissions Above 370 nm Due to Large Percentage of Heavier PAHs.

high component of heavier PAHs. The fluorescence of neat NTA product oil is shown in Figure 12. The NTA oil shows strong emissions at wavelengths above 350 nm where JP-4 emissions begin to decay rapidly. The increased emission is due to the larger percentage of PAHs in oil as compared to JP-4 and JP-5.

In both Figures 11 and 12, the BTEX signal is weaker, relative to the naphthalene component, than for the aqueous solution conditions. This result is as expected since the greater aqueous solubility of BTEX components over the naphthalene causes the BTEX to be preferentially dissolved. The major weight fraction of JP-4 is attributed to alkane, so neat JP-4 could reasonably be viewed as similar to a solution of BTEX and naphthalene in an aliphatic solvent such as cyclohexane or n-heptane.

For comparison purposes, the spectrum of JP-4 in water is compared to the neat JP-4 fluorescence in Figure 13. The wavelength shift is significant but thoroughly consistent with the somewhat different solvent environments. A large change in fluorescence intensity between the neat and dissolved phases is not revealed due to the normalization to peak intensity.

5. Spectra of Fuels Mixed with Soil

North Tank Area soils at natural moisture content were loaded with JP-4 and Fuel Oil; JP-5 was not considered within this test matrix due to its similarity to JP-4 fluorescence. For the 1 percent loading (mass/mass) used, fuel mixed with soil is likely to have three major phases: absorbed phase (accumulation of fuel compounds at the soil particle surfaces), neat phase (residual saturation within the soil voids), or dissolved phase (within soil moisture). The fate of fuel components retained by soils is not well understood.

Several features are notable in a comparison of the normalized fluorescence spectra of JP-4 on soil and in water (Figure 14). The fluorescence occurs at a wavelength approximately 10 nm shorter for the solution conditions than the soil conditions. The BTEX fluorescence relative to the naphthalene component is diminished for the soil environment. One possible reason is that BTEX is preferentially absorbed into internal sites compared to

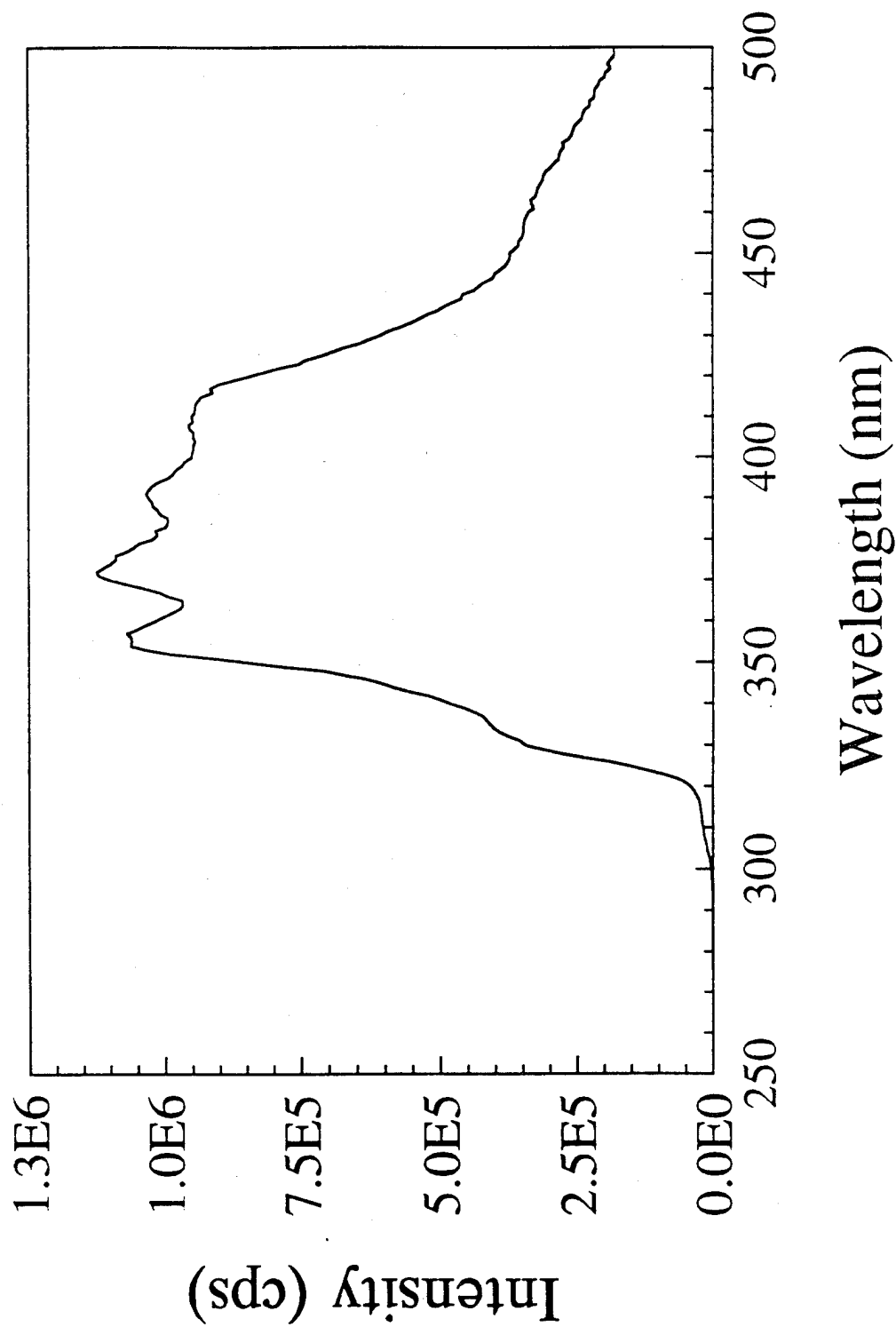


Figure 12. North Tank Area Emission Spectra. Note Increase in Larger Wavelength Emissions as Compared to JP-4. Increased Emissions Due to Higher Percentage of Heavier PAH's.

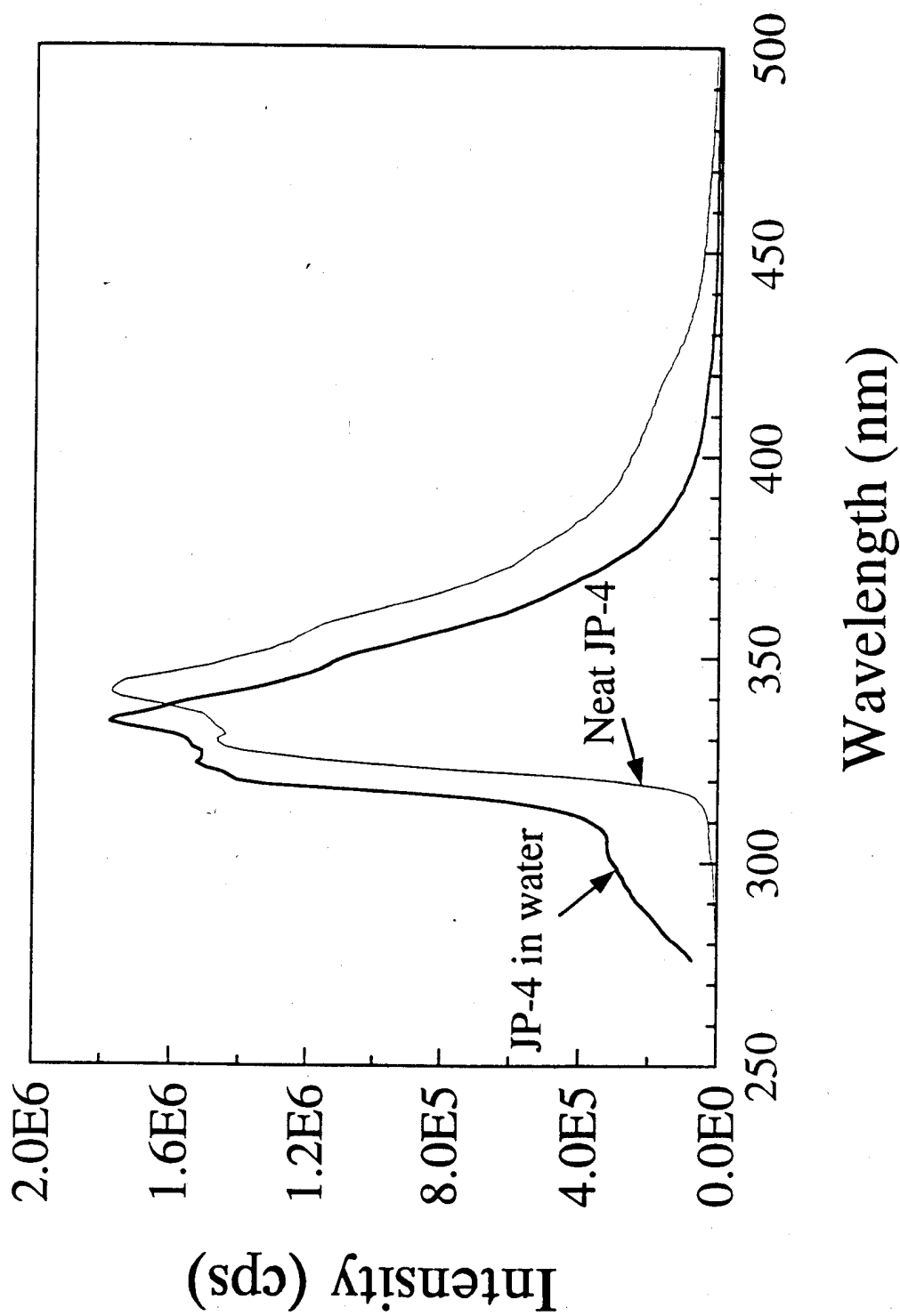


Figure 13. Comparison of Neat and Aqueous Phase JP-4. Note Shift in Spectra of Aqueous Phase JP-4.

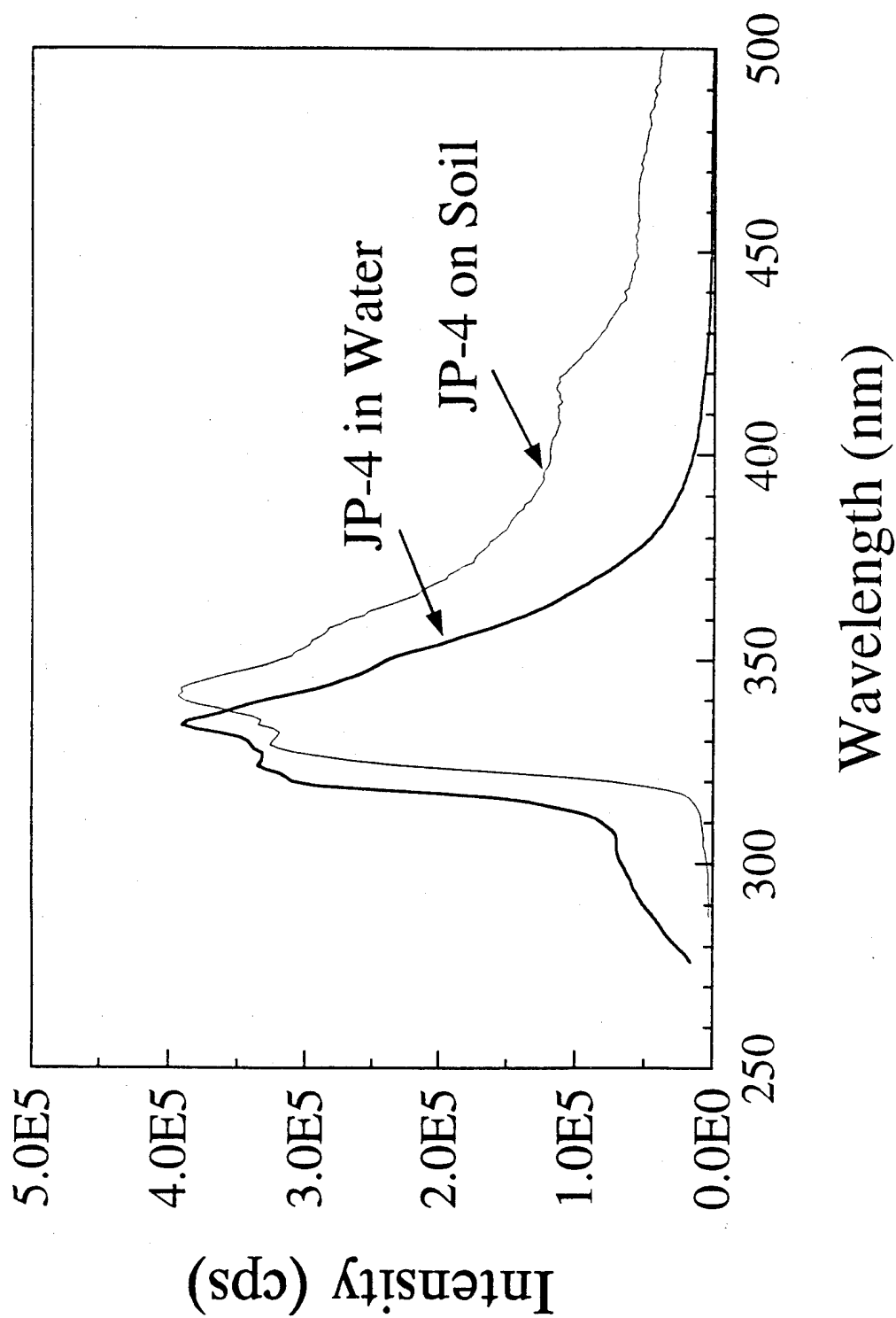


Figure 14. Comparison of 1% JP-4 in Water and in Soil. Soil Spectra Shifted to a Longer Wavelength, Plus Increased Emissions Above 350 nm, Possibly Due to Humic Acids.

naphthalene. Note the greater emission at longer wavelength for the soil environment, including an obvious peak at 420 nm. Just as in the case for the recovered NTA oil, the original interpretation was that this was associated with the presence of high molecular weight PAH's that have a low water solubility. However, as discussed in Subsection E.6, the long wavelength emission may be associated with humic acid fluorescence.

Fluorescence spectra of the NTA fuel oil excited at 266 nm and 290 nm are shown in Figure 15. Varying the wavelength has almost no effect on the fluorescence. The spectrum is very different from that of the JP-4/JP-5. Based on the position of the fluorescence maximum, one might speculate that the emission is due to compounds with three aromatic rings, but the common members of this class, phenanthrene and anthracene, do not match the observed spectrum.

The NTA spectrum are rather featureless and essentially independent of the fluorescence monitoring wavelength. The minor peak near 325 nm probably arises from Raman scatter by water. Acquisition of life time fluorescence in the broad range between 280 and 320 nm will provide a good indicator of the presence or absence of NTA product oil contamination.

6. Influence of Humics

The contribution of humic acid fluorescence to the overall signal was recognized as a potential contributor to the longer wavelength signals observed in both the NTA product oil (see Figure 10) and in the JP-4 (see Figure 14) contaminated soil spectra. Initially it was not recognized that the NTA product tested may have been significantly altered migrating through the soil. The increased signal at longer wavelength was initially suspected to be due to hexane, which is part of the water solution leaching plastic from the sample bottles. The interpretation that some fluorescent species were being leached from plastic sample bottles was discarded when the same results were obtained with glass bottles. Finally no logical alternative existed to the conclusion that the presence of organic solvents "activates" the humic acid fluorescence by some not completely understood mechanism.

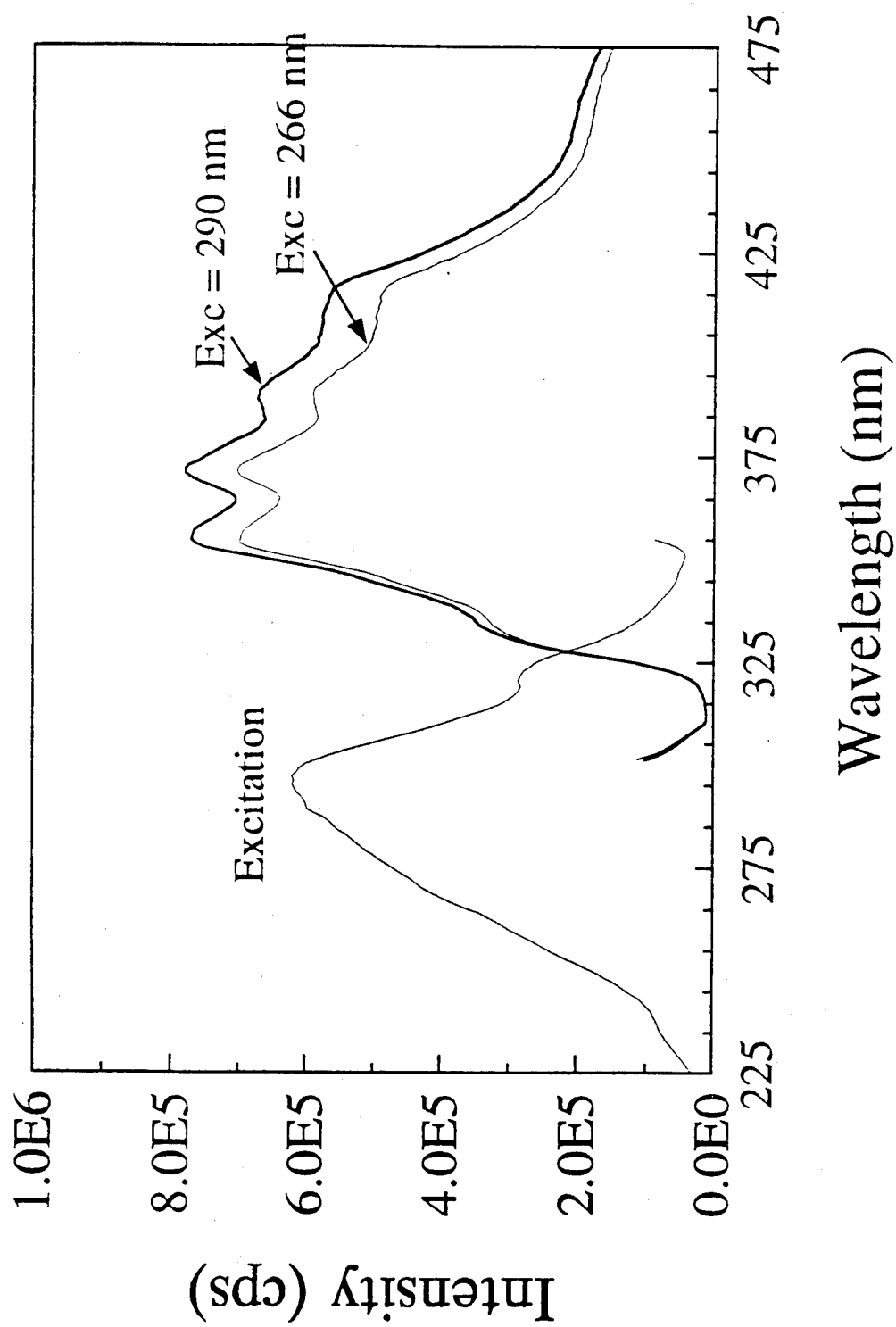


Figure 15. Comparison of NTA LIF Spectrum at Excitations of 266 nm and 290 nm.

Spectra were obtained of soil and soil spiked with 1 percent decane and heptane, which do not fluoresce. As expected, the control test with soil only shows no fluorescence, as shown in Figure 16. However, the decane and heptane spiked soil samples show strong fluorescence at 418 and 440 nm, which is believed to be humic acid fluorescence. This "structure" is actually an artifact of the wavelength response of the detection system on the Spex instrument. The actual maximum fluorescence intensity is near 440 nm, close to the value of 450 nm reported in Reference 10 for their cone penetrometer work. It is believed that the solvents leached humic acids from the soil matrix and that the fluorescence response is due to humic acids. This effect is not well understood, but will have important consequences for longer wavelength lasers. There appears to be a strong possibility that the "DFM equivalent" fluorescence that is consistently found using 337 nm excitations is in part due to humic acid. Since the humic fluorescence is apparently activated by the presence of liquid organic, there may well be a qualitative relationship between the humic signal and the presence of fuel contamination. However, this correlation will be highly variable depending on the soil type and amount of humic acid present in the soil.

7. Comparison of 337 nm and 266 nm Excitation

For JP-4 absorbed on soil, there is LIF emission that can be excited at 337 nm (the nitrogen laser wavelength) as shown in Figure 17, in contrast to the aqueous solution case. The emission shows peaks at 410 and 465 nm, much as observed in Figure 16, which was attributed to humic acids. Comparison with the fluorescence spectrum excited at 266 nm shows that much higher signals can be realized with the shorter wavelength excitation. In addition, the spectrum excited at 266 nm has a defined structure, which is due to naphthalene. The 266 nm LIF spectrum does show the 416 nm bump in the spectrum, but it is minor compared to the response at 337 nm.

8. Problems with Reproducibility

Failure to achieve reproducibility in the soil sample preparation was a key problem. The testing method was modeled after the procedures used by the NOSC group. Even with soil

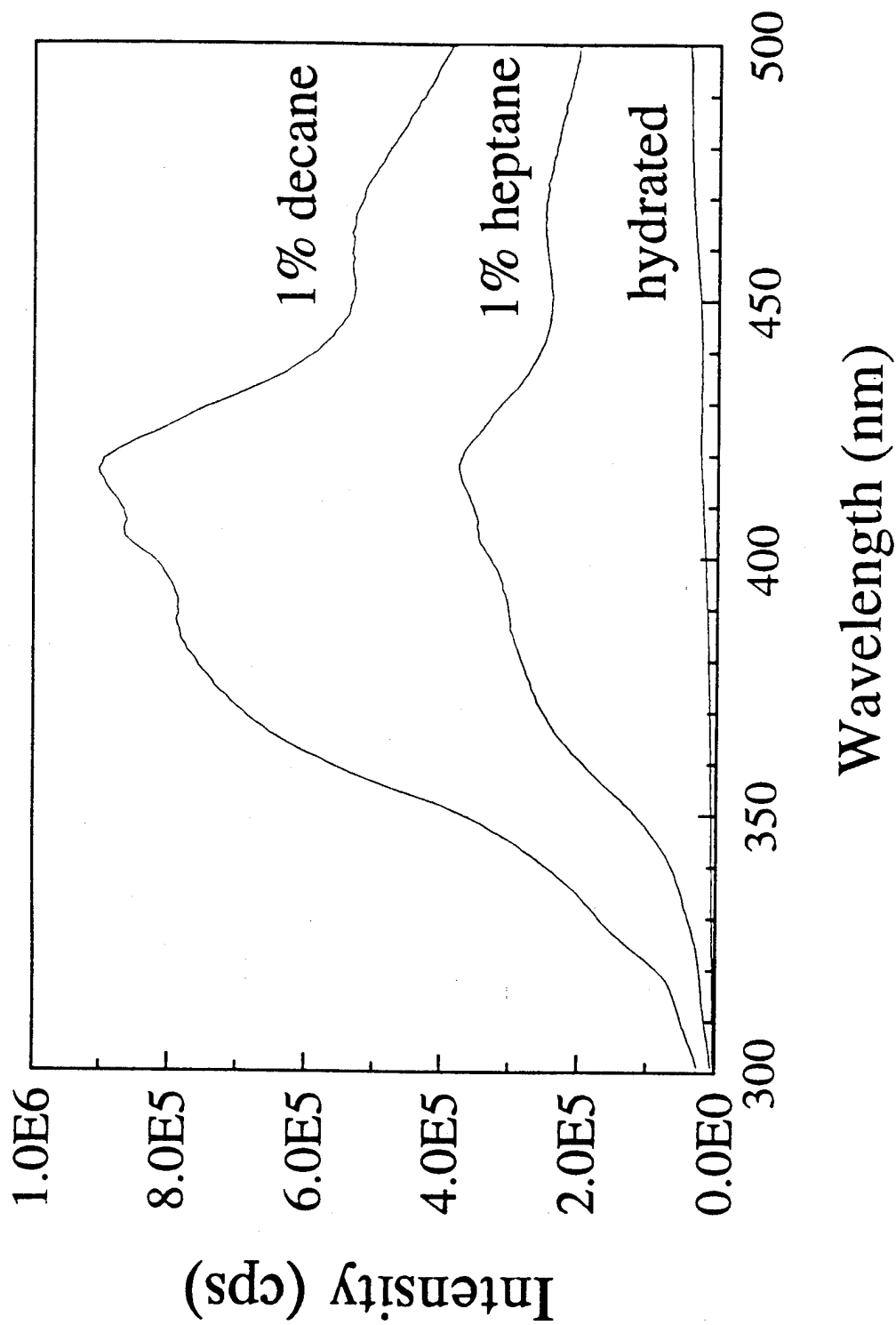


Figure 16. Fluorescence Signal for Soil and Soil with 1 % Each of Decane and Heptane. As Decane and Heptane Fluorescence is Due to Some Other Mechanism, Most Likely Humic Acids.

JP4(ARA) on soil\X266
JP40S-J(X337) times 5

JP40S-A.SPT
TEST7.SPT

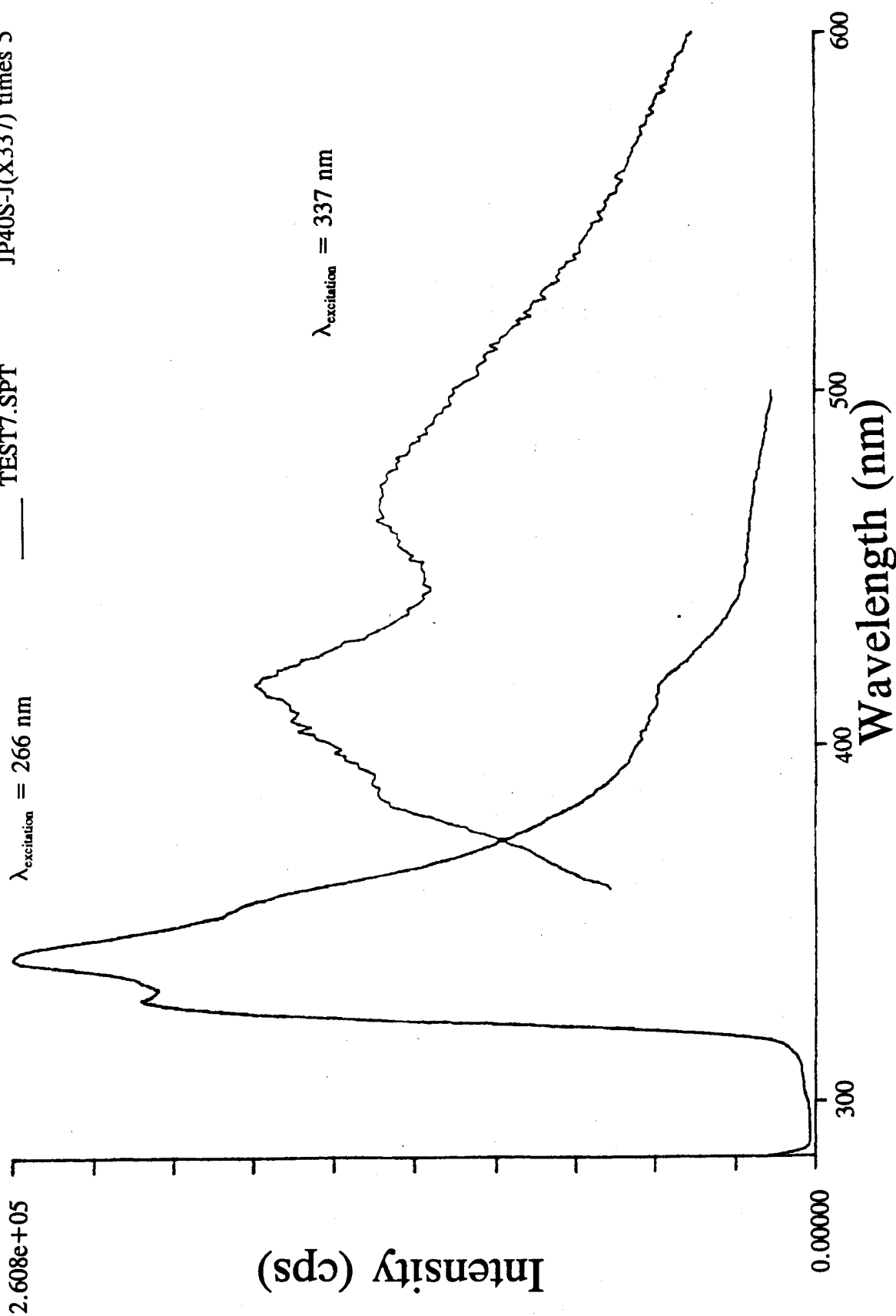


Figure 17. Comparison of JP-4 on Soil LIF Response With 266 and 337 Excitation. (Note: LIF Response with 337 nm Excitation Multiplied by 5 to Make Comparison.)

treated as outlined in the test plan (drying, sieving, addition of water, tumbling, spiking, tumbling), hot spots (regions of high fluorescence intensity) could be observed visually when the sample was excited in ultraviolet. Relative intensity variations by a factor of five or greater for different portions of the same sample were not uncommon. Some spectral variations (changes in shape of spectrum) also were observed.

At a loading of 1 percent JP-4 on the prepared NTA soil, there is a strong naphthalene-like fluorescence between 320 and 400 nm with humic acid fluorescence seen at longer wavelengths. Based on the intensity for the 1 percent sample, one ought to be able to see sample concentrations on the order of 0.01 percent but this proved impossible. A working hypothesis is that initial fuel loading "occupies" non-fluorescent sites on the soil (absorbed phase?) and only after these sites are "filled" does additional fuel loading lead to fluorescence. The crossover point is probably at 0.5 percent or less, but the poor reproducibility precludes a more precise determination. It is not clear whether the same behavior (intensity versus concentration) applies to true environmental samples; aging may well be necessary. Tumbling time is almost surely a critical variable.

Fluorescence signals for JP-4 on the NTA soil are extremely sensitive to air exposure, even under quiescent conditions. Figure 18 shows good fluorescence signal for a 0.5 percent JP-4 sample prepared according to the specified protocol. The sample was transferred to a Petri dish and exposed to the air for 30 minutes. The intensity across the entire spectrum was reduced but more so in the fuel signal region. After another 30 minutes, the signal was reduced to close to background levels. It is surprising that naphthalene sublimates (vaporizes) so quickly, but apparently it does.

Based on the limited laboratory testing conducted under this effort it became apparent that development of a repeatable, accurate laboratory testing method is required. The methods used on this effort, which were modeled after those used by the NOSC proved to be inadequate for clayey soils, and the tumbling process resulted in volatilization of a significant quantity of the lighter organic compounds. A systematic evaluation of instrument stability, accuracy and reproducibility will not be possible until these laboratory testing methods are developed.

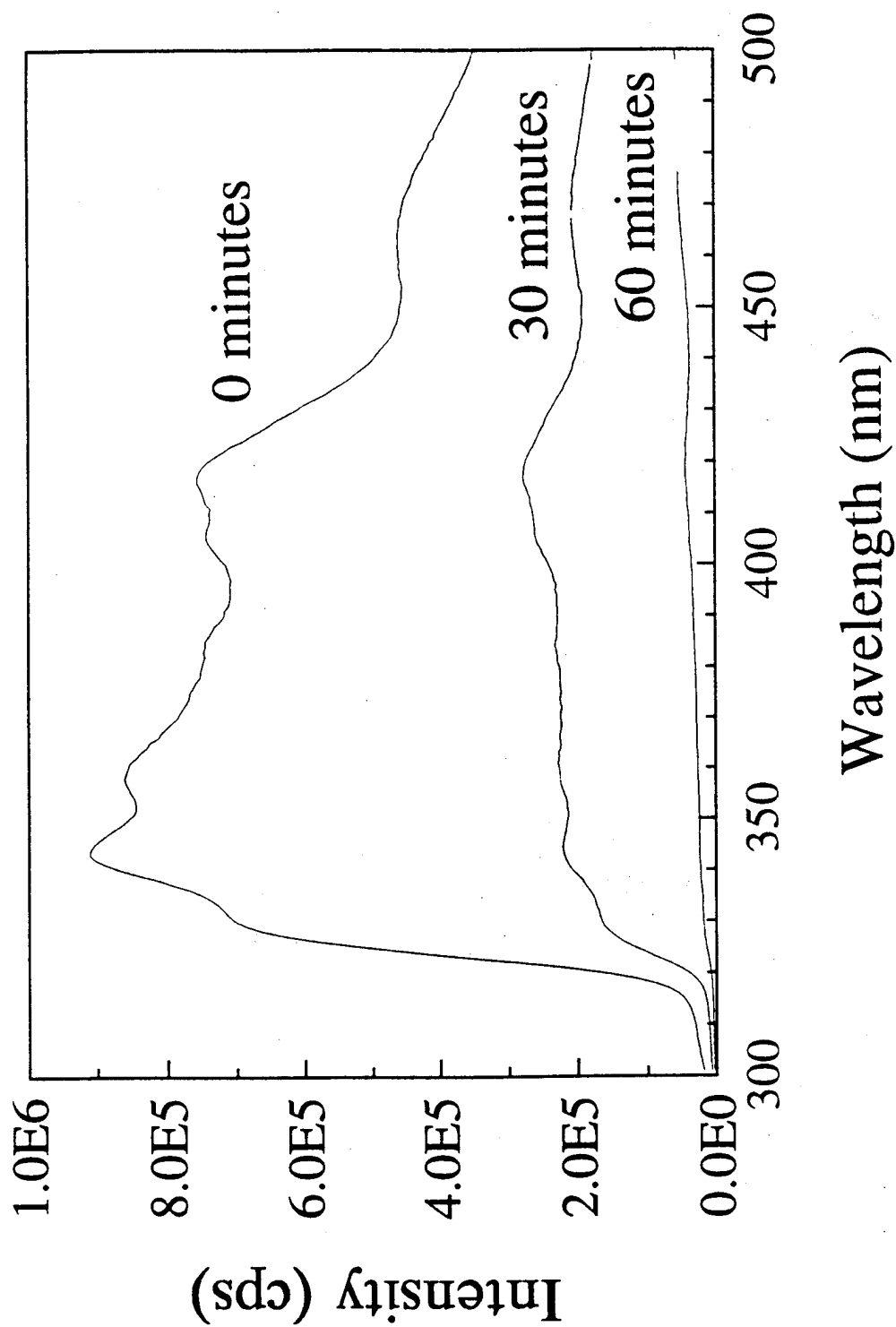


Figure 18. Effect of Exposure Time on JP-4 Spectral Signal. Samples Were Exposed to the Atmosphere at Room Temperature.

9. Effect of Compression

One of the questions to be addressed under the laboratory testing program was the effect of soil compression at the CPT soil interface on the LIF signal. In one set of experiments there was a pronounced increase in intensity as the sample was compressed in the soil mold. A twofold increase in LIF intensity was observed as the porosity was reduced from 50 percent to 20 percent. In another experiment, little variation was observed. However, given the variability in spectra from a single test, no conclusion can be drawn at this time. Addressing the effect of compression and reduction in soil porosity cannot be accomplished until adequate laboratory testing methods are developed.

SECTION V

EVALUATION OF LIF-CPT PROBE UNDER FIELD CONDITIONS

A. INTRODUCTION

The field demonstration and evaluation program had several objectives with the major objective being demonstration of a CPT deployed LIF system that could be used to locate fuel contaminated soils to at least the regulatory limits of 100 ppm, and potentially below these limits. Previous work by Gillispie (7) has demonstrated that the lower bound LIF detection limit for the aqueous phase is on the order of 100 ppb for toluene. The detection limit in soils was expected to be higher due to the increased complexities such as variability in soil type, soil grain size effects, humic acids and the influence of time on the fuel degradation. Laboratory studies to date have been conducted with fresh fuels; the influence of natural degradation on the fuel in soils has not been evaluated. Parameters which were evaluated in the field testing program and presented in this section include; evaluation of the system reliability, stability and repeatability, correlation of LIF-CPT intensity to contaminate concentration and evaluation of the sources of data scatter in the chemical and LIF-CPT data. Additional objectives included evaluating the cost effectiveness of the LIF-CPT system and demonstrating that LIF-CPT data coupled to a field deployed three-dimensional graphic representation system could be used to make near real time decisions regarding location of additional soundings, the areal extent of the plume and sources for the plumes.

1. Section Organization

Presented in Subsection B is a brief discussion of the Fuel Purge Area (FPA), which was selected to conduct the evaluation of the LIF-CPT probe. A complete discussion of the FPA investigation is presented in Volume II. A discussion of the LIF-CPT field techniques is contained in Subsection C, followed by a discussion of the system reliability and stability in Subsection D. Correlation of the analytical laboratory data is presented in Subsection E, along with a discussion of the data quality. A discussion of the uncertainties in the LIF data is presented in Subsection F and Subsection G presents two- and three-dimensional graphic

representations of the data. Subsection H contains an analysis of the cost effectiveness of the LIF-CPT system, and Subsection I summarizes the conclusions drawn from analysis of the field data.

B. FUEL PURGE AREA SITE DESCRIPTION

The Fuel Purge Area was designated as the key test area to demonstrate the ability of the LIF-CPT probe to characterize JP-4/JP-5 contaminated soil. The field program for the Fuel Purge Area was essentially doubled from that presented in the DT&E plan to accomplish this objective. A total of 55 LIF-CPT profiles, 15 soil sample locations yielding over 60 soil samples from both CPT probing and drilling, and 6 water samples retrieved from drill holes were accomplished (see Volume II for details). Total LIF-CPT footage for the test area was 927 feet, approximately 60 percent of the demonstration program total.

As shown in the site plan (Figure 19), the Fuel Purge Area encompasses over 5 acres in the east central part of Tinker AFB. The active tarmac is located just to the north. No formal investigations of the site have been conducted and only minimal data was available at the beginning of the investigation. Several sources of JP-4 and JP-5 fuel contamination are known to exist at the FPA, including the fuel hydrant system located 50 feet off the apron, two 30,000-gallon fuel purge USTs and a drainage sump UST, waste fuel/oil aboveground cylindrical tanks, and the waste fuel dump turnaround area.

Spills are known to have occurred during the last 2 years as fuel is off-loaded from bousers to the storage bunkers. The bousers are pulled from the tarmac using trucks, rolled onto the turnaround pad and onto the ramp. The ramp lies above a storage bunker that drains by gravity to the above-ground tanks located 300 feet south. The old ramp was the site of spills around the bunker onto bare soils. Previous characterization efforts consisted of hand probing and TPH, BTEX and TCLP analyses that defined the extent of soil contamination around the ramp. A volume of 2,820 cubic yards in a 100 feet by 50 feet area was determined to have TPH values in excess of 50 mg/kg (Reference 11); contamination did not exceed a depth of 10 feet in most of the probes. About 350 cubic yards of grossly contaminated soils located beneath the bunker

Fuel Purge Area (Tinker AFB, OK)

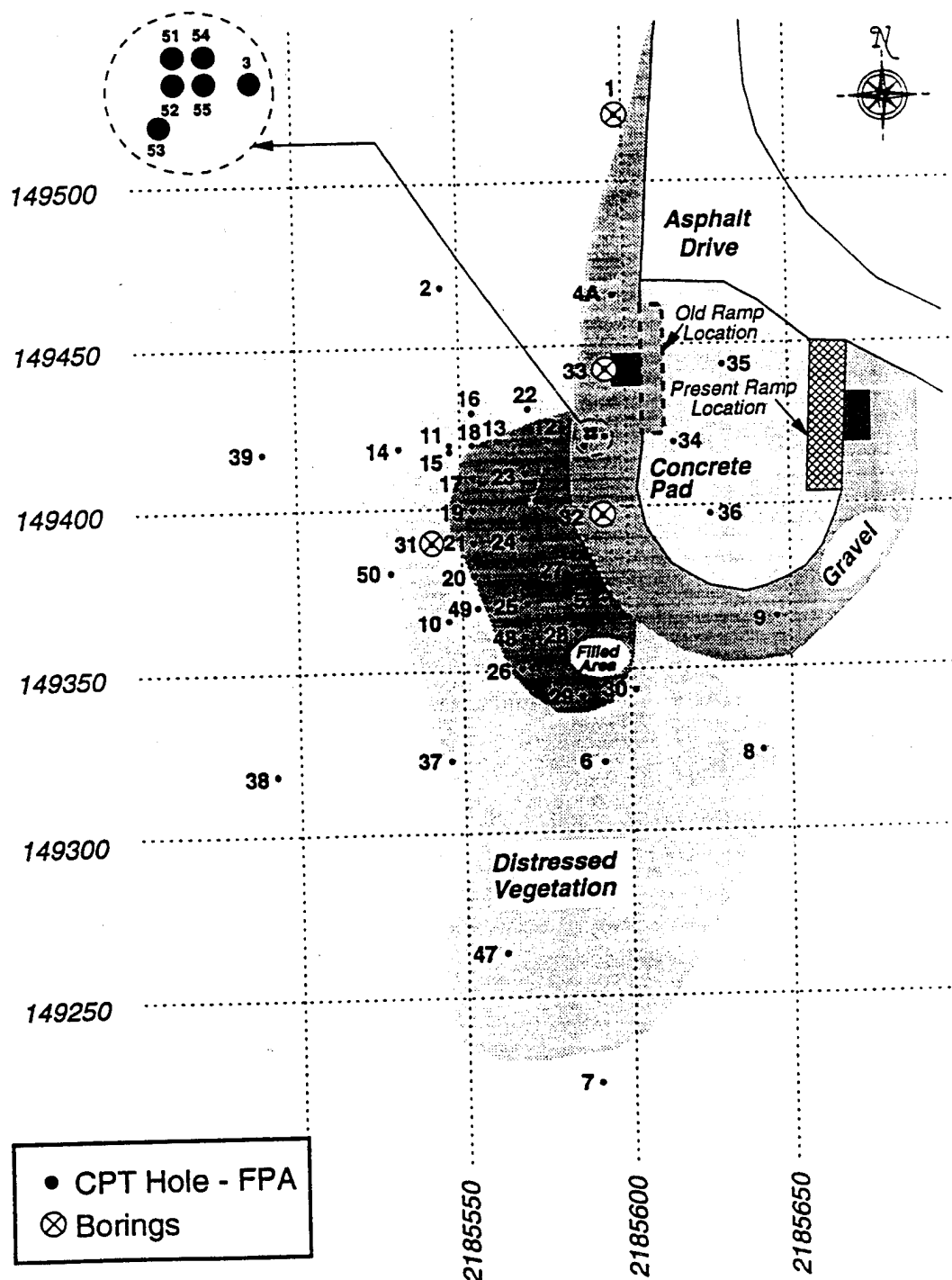


Figure 19. Layout of LIF-CPT and Auger Sample Boring at Fuel Purge Area, Tinker AFB, OK.

were reportedly excavated and disposed off-site during dismantling of the old facility. The new fuel turnaround dump facility includes concrete spill containment dikes around the bunker.

Soil chemical results for the fuel dump turnaround are summarized in Table 2. CPT sampling locations used in the table were FPA-03, 04, 05, 11, 12, 13, 20 and 47, and the drill holes used were FPA-B01, B31, B32 and B33. The most notable item is that all 47 samples tested for TPH had detectable amounts, although 19 had TPH values of less than 50 mg/kg. About half of the samples tested had detectable quantities of BTEX or naphthalene. Some chlorinated solvents tested positive, suggesting a contaminated or waste fuel was spilled.

As discussed in Subsection H, site reconnaissance and LIF-CPT profiling revealed that a surface spill recently took place in an area located west-southwest of the new pad. The portion close to the gravel drive had been filled with a few inches of soil to reportedly cover a wet spongy area. This covered area is surrounded by a larger area of distressed vegetation that extends about 100 feet to the south. Surface drainage is mostly directed to the south by a 1 to 2 percent slope. An extensive characterization of this suspected spill area was conducted. As discussed in Subsection G, a separate spill was clearly identified using the three-dimensional visualization; this spill was not known to exist before this effort.

C. OPERATION OF THE LIF-CPT SYSTEM

The LIF system is controlled by an independent computer and networked with the standard ARA CPT computer, which is used to obtain standard CPT data of tip stress, sleeve stress, and pore pressure. The test is initiated by calibrating both the LIF and CPT parts of the probe. The LIF is calibrated by holding a standard solution of 2.5 percent JP-4 jet fuel in hexane up to the window and setting the LIF response to 4,095. The CPT tip, sleeve and pore pressure instruments are calibrated using standard operating procedures. Based on the laboratory studies, the tunable dye laser was set to produce 290 nm excitation during the push, and the emission monochromator was normally set at 340 nm. The laser required a one-half hour warm-up, similar to the CPT hardware components.

TABLE 2. CHEMICAL SUMMARY OF FUEL DUMP TURNAROUND AREA SOIL SAMPLES

Parameter	Units	Number of Times Detected/Total Samples	Stations Detected/Total Stations	Range of Concentrations	Detection Limit
TPH	mg/kg	47/47	12/12	12 - 22,000	10
Benzene	ug/kg	15/41	9/12	20 - 4,300	20
Toluene	ug/kg	23/41	9/12	20 - 8,300	20
Ethyl Benzene	ug/kg	22/41	9/12	20 - 3,600	20
M-Xylene	ug/kg	29/41	10/12	20 - 33,400	20
Naphthalene	ug/kg	28/41	11/12	20 - 3,600	20
2-Me-Naphthalene	ug/kg	28/41	11/12	20 - 39,000*	20
T. Phenols	mg/kg	3/9	3/11	1 - 6	0.4 - 5
Trichloroethene	ug/kg	2/12	1/9	5 - 1,000	5
1,1,2,2-Tetrachloroethane	ug/kg	1/12	1/9	5 - 9	5

Once the probe is calibrated, it is lowered to the ground surface. The probe is pushed into the ground at a constant rate by two hydraulic push cylinders. Measurements of tip stress, sleeve stress and pore pressure are made at an interval of one sample every second, whereas the LIF data is acquired at one sample every 4 seconds. The LIF data being measured during the pushing phase is the area under the time decay curve of the fluorescence response at an emission wavelength of 340 nm. The data is continually acquired whenever the probe is moving.

A fluorescence "count" is defined as the area under the fluorescence waveform that is equal to 1 bit (1/4095) of the area under a standard waveform of 2.5 percent JP-4 jet fuel in hexane measured prior to testing. In other words, a fluorescence count of 2,047 would indicate that the integrated contaminant waveform would have one-half the total fluorescence area under the waveform (the integrated waveform) as the standard produced. While this "count" system does not take the background signal and rise time information into account, it does serve as an excellent "coarse" indicator of contaminant fluorescence, and thus, concentration.

The LIF-CPT system takes advantage of both "active" and "static" modes provided by cone penetrometer testing. Using a constant excitation wavelength, the push mode enables spectral or time-resolved LIF data to be collected at regular depth intervals along with the CPT data (tip stress, sleeve stress and pore pressure). The Tinker laser spectrometer was set up to provide time-resolved fluorescence waveforms at 340 nm during the push. Since fluorescence is a stochastic process, multiple laser shots were averaged to improve the definition of the LIF waveform. It was determined that averaging 16 waveforms was adequate for the LIF-CPT. About four seconds were required to average the waveforms and download the data to computer memory. The LIF data were downloaded to two file types: normalized intensity (counts) that was transferred to the CPT control computer, and the actual waveform data that was stored on the LIF control computer hard disk. The fluorescence waveform data could be used for further analyses such as lifetime or intensity measurements.

When areas of significant concentration were encountered, the fluorescence technician signaled to the CPT operator to pause the push. At this point the technician acquires a WTM that contains both time and wavelength information about the contaminant fluorescence. This

additional information may prove useful for determining the source of the contamination, the humic acid background, and to some degree, the individual chemicals that make up the contamination.

A typical LIF-CPT profile is presented in Figure 20. Shown are the tip and sleeve stress profiles along with the pore pressure profile. This information is useful in determination of soil stratigraphy which is shown on the right side of the figure. For this location the soils consist of mostly sands and silty sands, with two thin sandy clay seams at elevation 1,278.5 and 1,275 feet respectively. Also presented is the LIF profile that shows contamination throughout the unconsolidated materials. Two thin layers of high contamination are shown at elevations 1,284 and 1,276 feet. It is interesting to note that the LIF response returns near baseline at an elevation of 1,275.5 feet, which corresponds to a strength increase of the material as indicated by the tip and sleeve stresses.

The vertical resolution of CPT profiling is governed by the data retrieval rate and the penetration rate. The retrieval rate is about one per second for ARA's CPT data acquisition system. The push rate is normally set at a nearly constant value between 1.5 to 2.5 cm/s (ASTM specifications). Using a 2 cm/s push rate yields a CPT data point about every 0.05 feet. Due to the slower retrieval rate, a LIF data point would only be acquired every 0.20 feet. Thus, consideration was given to slowing the push rate down to obtain a high vertical resolution; this would also significantly affect production rate.

Static mode measurements were occasionally obtained when the probe was stationary (typically at 1-meter depth intervals due to required rod additions) or at particular points of interest. The static mode allows generation of multidimensional matrices of LIF data, such as wavelength-time matrices (WTM). A total of about 50 WTM's were collected during the Tinker AFB DT&E. The same excitation wavelength used in the push mode was used in generating the WTM's (290 nm). Each WTM consisted of 20 waveforms collected at 10 nm intervals between 300 nm and 500 nm emission. Two-hundred and fifty-six (256) traces were averaged to produce each waveform. Using these settings, the WTM measurement took approximately 5 minutes to perform.

FPA-11

09/14/92

North 149420. East 2185547.

Elevation 1285.5

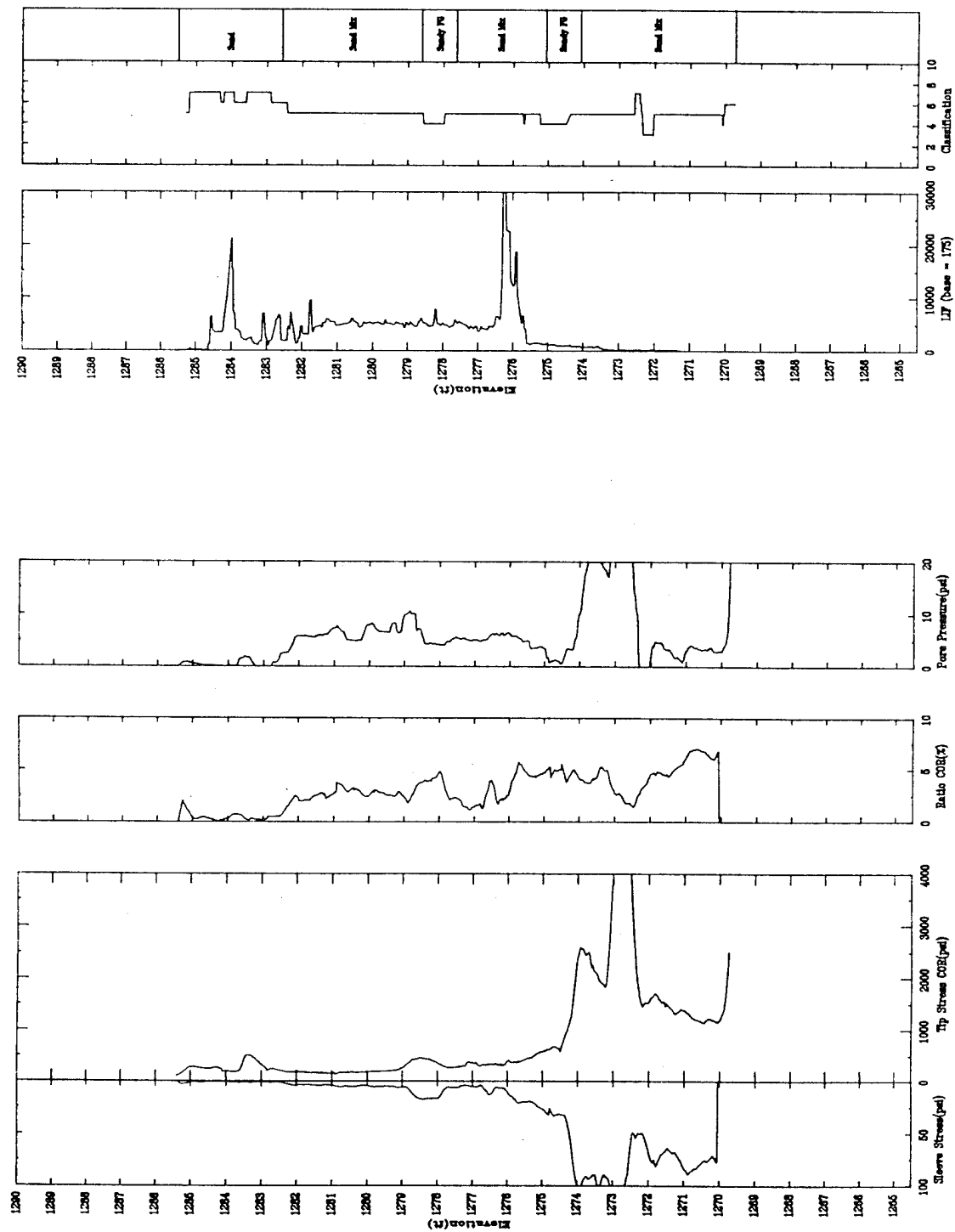


Figure 20. Typical LIF-CPT Profile from Fuel Purge Turnaround Area.

CPT pore pressure dissipation tests were occasionally performed in conjunction with the LIF measurements. Dissipation data is used to determine water table depths and hydraulic conductivities (for soils with $K_h < 1 \times 10^{-5}$ cm/s).

D. RELIABILITY, STABILITY AND REPEATABILITY

One of the primary concerns of any new instrumentation is the reliability, stability and repeatability of the system under conditions to be encountered in the field. While formal evaluations of the LIF prototype systems have yet to be made, qualitative evaluations were made of the two major components of the LIF system: the laser system in the CPT truck and the LIF-CPT probe.

Overall, the laser system was quite reliable, with little down time. Concern had been expressed about the optical system becoming misaligned due to the rough ride in a CPT vehicle as it traversed a site. Components of the system were individually shock isolated; however, once in the field additional shock isolation was required for the breadboard on which the laser and optics were mounted. Once this was accomplished, occasional adjustments were needed, only when traversing extremely rough terrain.

Only one laser component, a dye cell, failed during the LIF field testing program. A hairline crack developed in one of the cells, which increased the baseline on a portion of the soundings. Once the cell was replaced the baseline returned to normal; however, some of the LIF pushes at Tinker had excessively high baseline due to the cracked dye cell. The crack in the dye cell was not discovered until late in the program.

The only unexpected environmental problem was that the laser power pack generated more heat than expected and the truck air conditioning system was not large enough to meet the increased cooling demand of the LIF system. This led to some heating problems of the system that primarily effected the LIF baseline. Incorporation of a LIF-CPT system in a CPT truck must account for this increased heat load. In addition, the laser requires 220 volt power that is not commonly available on many CPT trucks.

Similar to WES's findings, the concept of fiber-optic delivery and collection using a sapphire window is sound. The window appears to be of sufficient strength to withstand the cone environment. "Smearing" of contaminant or soil on the window did not appear to be a major problem as distinct layers were defined by the LIF data. However, this was not quantified in any manner.

The most serious problem encountered was the reliability of the LIF probe, particularly alignment of the six-around-one fiber arrangement. As the instrumentation cable was handled, mechanical strain was induced on the fibers which caused the fibers to move in and out (termed pistoning) of the protective nylon jacket and which caused misalignment of the fibers at the sapphire window. The misalignment at the tip surface increased the amount of light scatter and possibly inducing fluorescence due to the nylon jacket. The inward pistoning of the plastic clad core was visible and was generally associated with the protrusion of the jacket from the connector. The plastic cladding or buffer is not bonded to the jacket and so is able to move in reaction to strain effects on the fiber optic. Small pieces of the nylon jacket were flaked off of the protective jacket and these fluoresced, increasing the baseline of the LIF signal. Strains induced by the tight radius may have caused degradation or fatigued the epoxy bond between the buffer and silica core and between the connector and the jacket, which would also contribute to the background. According to the manufacturer, large stress is associated the 1.25-inch bend within the laser module. Theoretical studies of the long-term strain resulting from the bend suggest that the fiber optic experiences stresses above the proof testing level. Thus, the tight bend is thought to be the source of stress causing the pistoning.

Because of the above straining, after a short period of use the baseline became unacceptable, necessitating field disassembly and cleaning of the probe by removing bits of nylon and moisture and then aligning the fibers, epoxying and grinding the face flat. Once this was accomplished, the baseline returned to acceptable levels and the testing continued, except for those tests conducted with the cracked dye cell. For these tests the baseline was quite high. As stated above, once the cracked dye cell was discovered, the baselines were reduced to 80 counts (out of 4,095 full scale).

Another source of error that was eliminated early in the program was soapy water used to lubricate the fibers as they were being inserted into the Teflon® tubing. The water dripped into the LIF probe window area as the push tubes were pushed into the ground. The high baseline on the prototype system can be readily eliminated by redesigning the mechanical connection of the fibers to the CPT probe and not using a lubricant on the fiber optic cables. In addition, the baseline drift due to heating of the laser system can be eliminated by specifying a larger cooling system in the CPT truck.

The high baseline did have an effect in developing a correlation of the LIF data to contaminant concentration. Many times the baseline was larger than the corrected signal, especially at low concentrations, making interpretation of the signal uncertain. For most instrumentation systems, one would like to have a baseline of 1 percent or less of the signal so that low level signals can be easily separated from the background noise. For much of the LIF data the baseline was significantly larger than the signal. In developing the correlation between LIF and fuel contamination, the LIF data that had a signal to baseline ratio of 0.5 or greater was not used.

E. CORRELATION OF LIF INTENSITY TO CONTAMINANT CONCENTRATION

One of the major objectives of the project was to determine if the LIF-CPT probe could be used to detect in-situ chemical contamination. The ability to detect high-level contamination has been demonstrated during the field investigation at Tinker, AFB; however, the sensitivity of the instrument is of primary concern. To evaluate the correlation of LIF intensity to chemical concentration, a limited data set of only high quality data from one site (the Fuel Purge Area) was used. Based on LIF soundings, the Fuel Purge Area was determined to contain two separate plumes of jet fuel contamination. The two plumes are approximately 10 to 15 feet in diameter and separated by approximately 40 feet between centers. Both plumes are the result of individual spills. A total of 53 locations were tested at this site in approximately 5 days using either LIF-CPT, CPT soil sampling or traditional drilling soil sampling methods. The samples were tested by both field gas chromatography and laboratory analytical chemistry methods to determine the degree of soil contamination.

During the field program, chemical testing of soil samples were performed to develop a data set that could be correlated to LIF intensity. The chemicals under study, based on the laboratory studies indicated that naphthalene and potentially 2-methyl-naphthalene were the primary source of fluorescence in soils. These chemicals were evaluated and determined not to be correlated with LIF response, discussed below.

To evaluate the relationship between LIF and naphthalene concentration, the baseline corrected LIF values were plotted versus naphthalene concentration. The naphthalene concentrations were those measured by the field GC laboratory. The results from the outside analytical laboratory (ANALAB) were not used because only six samples were tested and only three had measured concentrations above the detection limit. The ANALAB data represents a data set that is too small to be of use for evaluation purposes. Figure 21 presents the comparison between the field GC naphthalene results and the baseline corrected LIF values. No trend is apparent in this data set, indicating that there is no relationship between the two values. Although, it was believed that a trend would be evident, since dilutions of naphthalene in water do show strong trends (Reference 7). Some possible reasons for the differences are that the LIF response is due to other chemicals, the influence of soil effects, or general inaccuracies in the data set.

Examination of the plot of 2-methyl-naphthalene versus LIF shows the same trend as for naphthalene. Once again, the data set of ANALAB results was too sparse to be of value (six samples, and only four values above detection limits). Figure 22 shows the LIF counts versus 2-methyl-naphthalene concentration based on the field GC results. Again no trend is evident, as the amount of scatter is high. Many of the possible reasons as to why the same trends as seen in water dilutions that apply to naphthalene are valid here and will not be repeated. Overall, it was surprising that neither naphthalene or 2-methyl-naphthalene showed any encouraging results, since the testing of diluted solutions was very encouraging. Additional laboratory testing should be performed to understand why the measurements were not as expected.

The final parameter that was evaluated was TPH. As discussed previously, TPH represents measurement of a large number of hydrocarbon compounds, many of which are the

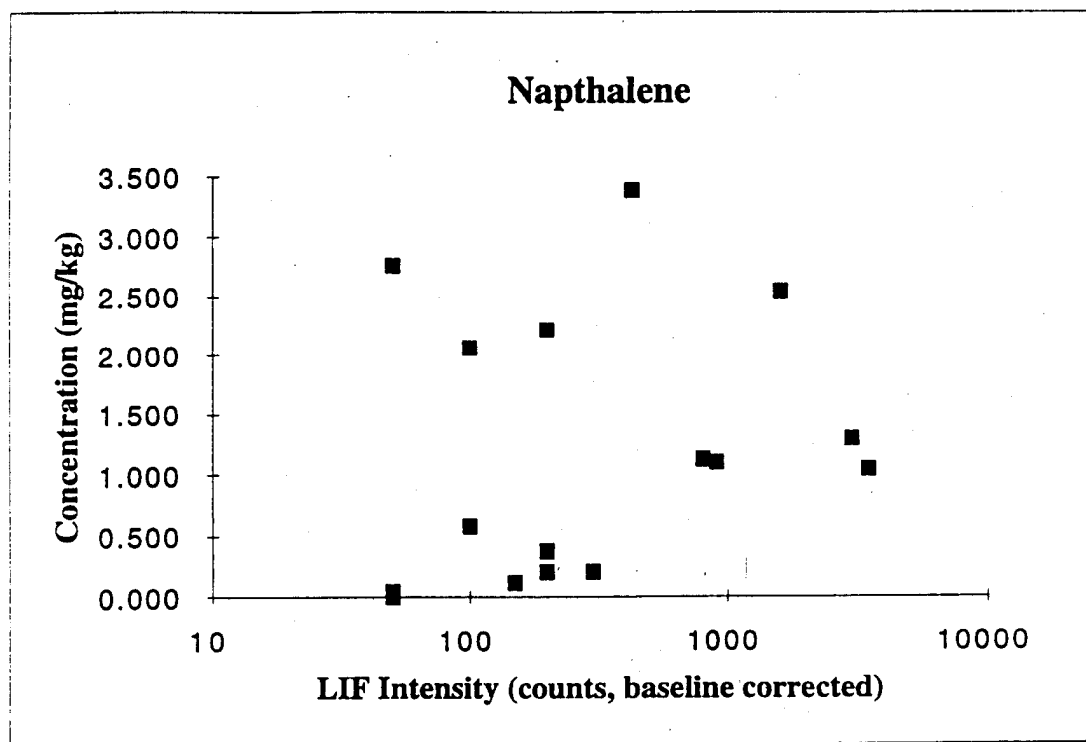


Figure 21. Comparison of Naphthalene Concentration to LIF Intensity for High Quality Data Set.

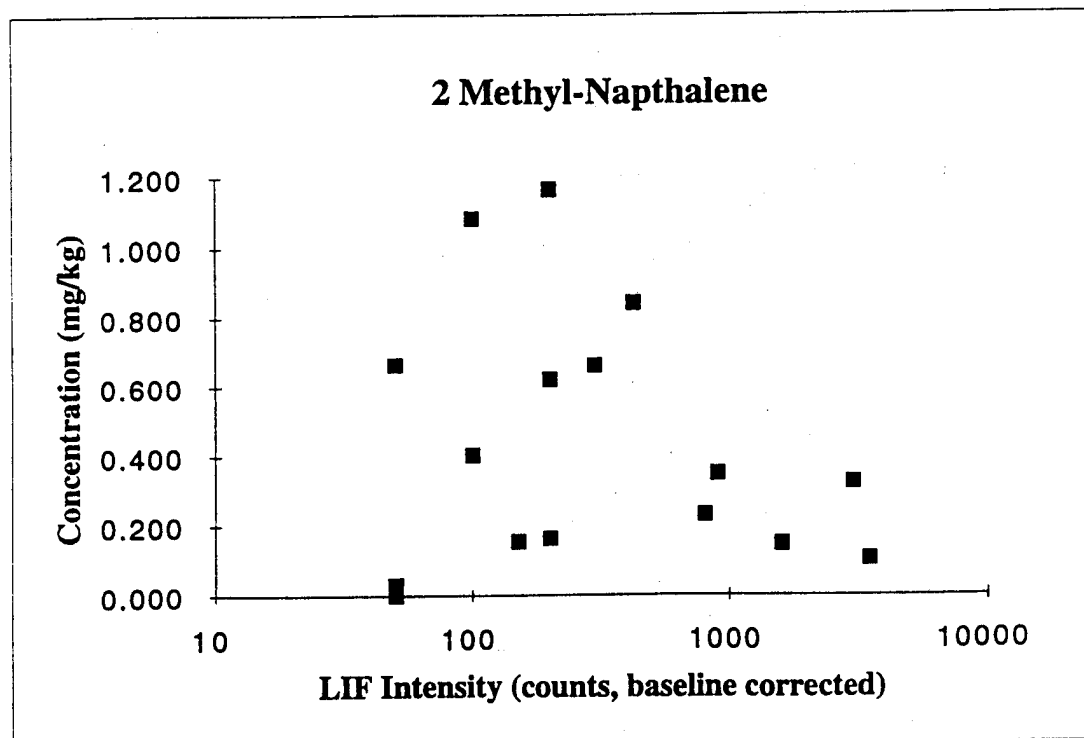


Figure 22. Comparison of 2-Methyl-Naphthalene Concentration to LIF Intensity for High Quality Data Set.

multiringed compounds. These compounds are known to fluoresce and make up a much larger percentage of jet fuels than the naphthalene and 2-methyl-naphthalene that comprise 0.4 and 0.3 percent of JP-4 respectively (Reference 12). Figure 23 presents the TPH and LIF values for the samples in the data subset which has a signal to baseline ratio of 0.5 or greater. This figure clearly shows a definite trend in the data indicating a relationship between the two parameters. A line of best fit was determined through the data and the resulting equation is shown in Figure 23. This equation has a reasonable correlation coefficient of 0.87, indicating a fairly good fit; however, there is considerable scatter in the data.

This same data subset was also compared to the entire data set collected during the field program in which samples were tested for TPH. This information is shown in Figure 24 with the open data points representing the data with a signal to baseline ratio of greater than 0.5 and the closed data points representing points with lower signal to baseline ratios. Once again, the trends present in the high quality data are also present in the low quality data, but with additional scatter.

In addition to the trends shown in Figure 24, there are two other important regions. These are the regions of false positive and false negatives. Since TPH of a 100 is a regulatory limit, tests where the TPH is above 100 will be considered a positive result and TPH values below 100 will be considered as negatives. Using the fit to the data, a TPH of 100 corresponds to a LIF of 95.6 counts baseline corrected. Based on this, the region of LIF above 96 will be considered a positive test and values below 96 as representing negative or indications of no significant contamination. Examination of the high quality data in Figure 23 shows one false positive and one false negative. Examination of the LIF profiles indicates that these data points are at the boundary between a zone of low and high degree of contamination and that the spatial variation may account for the false result. Examination of the lower quality LIF data set shows instances of the LIF indicating contamination, when none was indicated by the TPH data (false positive) and LIF indicating no contamination when the measured TPH is above 100 (false negatives). The percentage of false negatives based on the total data is 18 percent. This value is high by instrumentation standards. There are two known sources of bias that are causing at least part of the data scatter.

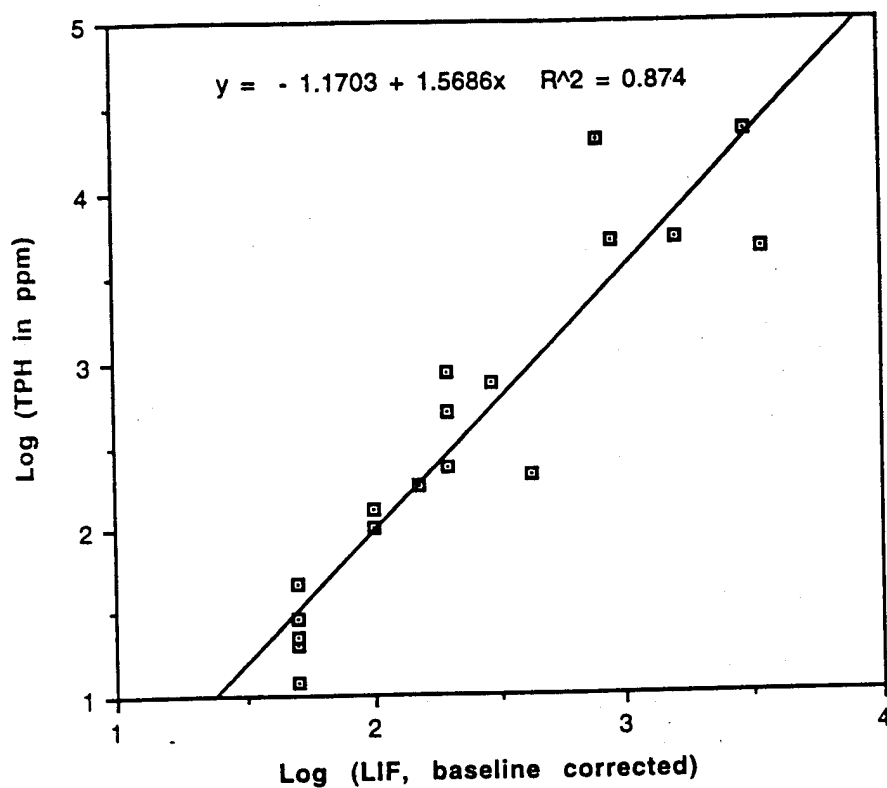


Figure 23. Correlation of TPH to LIF Intensity for Higher Quality LIF-CPT Data at Fuel Purge Area.

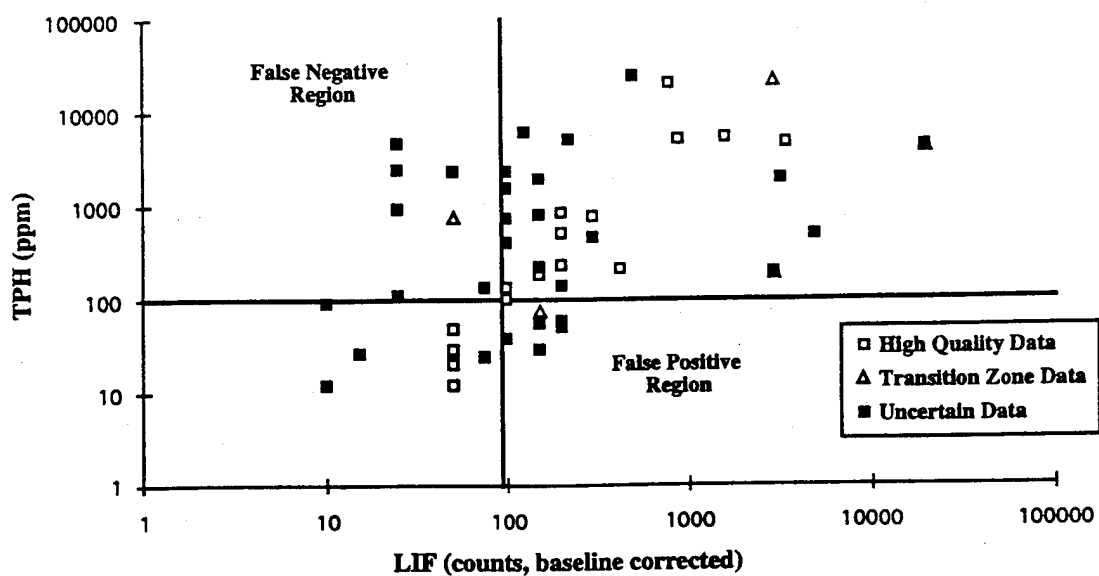


Figure 24. Comparison of All LIF-CPT and TPH Data at Fuel Purge Area. (Note Areas of False Positives and False Negatives.)

F. ANALYSIS OF DATA SCATTER

As with any field experiment, there are several possible sources for the scatter. Some of the different types that were present during the testing at Tinker, AFB were large sampling intervals, effects of soil mechanics, consistency of measured parameters (i.e. were all LIF responses from the same or different contaminants), variability in the analytical chemical analysis, and LIF-CPT test operating procedures. Some of these sources of scatter are controllable, whereas others are not and will be present during any testing program.

One probable source of data scatter is the large sampling interval, sometimes as large as 3 feet. The scatter occurs as the LIF measurements were made every 1 to 2 inches, whereas the sampling interval that was sent to the analytical laboratory typically ranged over 1 to 2 feet. The sample volume required by the analytical laboratory was typically one quart, which would comprise 1 to 2 feet of drilling core. All this core would be mixed together and tested to determine a TPH values. If only a thin seam of the soil was contaminated, the test results may have been diluted, and not representative of the thin seam that caused the LIF response. The laboratory test results were then compared to the average LIF measured over that interval. In the future, CPT soil sampling should be used to obtain samples from precise depths, and the smallest possible sample volume should be tested to determine contamination. The CPT soil sampling methods are more precise than traditional drilling methods for determining the sample locations, and generally have nearly 100 percent sample recovery, as opposed to 70 to 80 percent for drilling techniques.

The second improvement that can be made to reduce scatter would be a better understanding of the effects the soil may be having on the LIF signal, and any potential corrections that may be needed to reduce or compensate for these effects. The first step along this process was performed during the laboratory testing program phase of this project. However, this initial program has just begun to investigate the effect of soil on LIF. Key parameters that need to be evaluated in the future include the effects of soil type, soil moisture and soil compression as the CPT passes through the soil.

In this analysis no estimates of exactly what chemicals were present were made. The WTM's or the FVD's (LIF time decay curves versus depth) indicate some trends are present, as discussed in Volume II in the site analysis section. At this stage of development the LIF can indicate with a high degree of confidence that petrochemical contamination is present. Analysis of the WTM's shows some differences between the different sites. At the North Tank Area the typical peak wavelength was 360 to 410 nm (see Figure 25) for locations on the north side of the fuel oil tank. At the Fuel Purge Area, the peak wavelength was 340 to 360 nm, as shown in Figure 26. These same trends were as expected, since the laboratory study of neat material identified the same trends between fuel oil and jet fuels. The WTM's measured at the Fire Training Area (Figure 27) also shows trends that are consistent with jet fuel contamination. This simplified analysis indicates that general fuel types can possibly be determined by the LIF, although additional work is clearly needed to further advance the methods.

The above evaluation of the LIF-CPT probe was based on the assumption that the LIF response at the FPA was due to jet fuels. All the WTM's presented in Appendix J of Volume IV support this assumption. If different types of contamination were present, they would certainly introduce additional scatter in the data. Other chemical aspects that might have effected the LIF evaluation, would be whether or not the LIF is more sensitive to one chemical than another, indicating a preference that could be compensated for in the analysis.

Finally, additional study of the LIF-CPT operating procedures should be performed to reduce any variabilities. One operating parameter identified as significant during the field testing program was penetration speed. The results of this study showed that the tip stresses were not influenced by penetration rate, but the sleeve stresses and pore pressures were slightly increased by the slower push rate. A test plan of the five pushes conducted as a part of the experimental series is shown in Figure 28. Figure 29 presents the tip stress profiles, that are consistent across section A-A of the experimental series. The tip stresses are consistent in all three profiles, even though locations FPA-52 and FPA-03 were conducted at a slow rate of 0.5 cm/sec, and FPA-55 was conducted at a rate of 1.5cm/sec.

North Tank Area
NTA-05, Depth = 12.75 ft

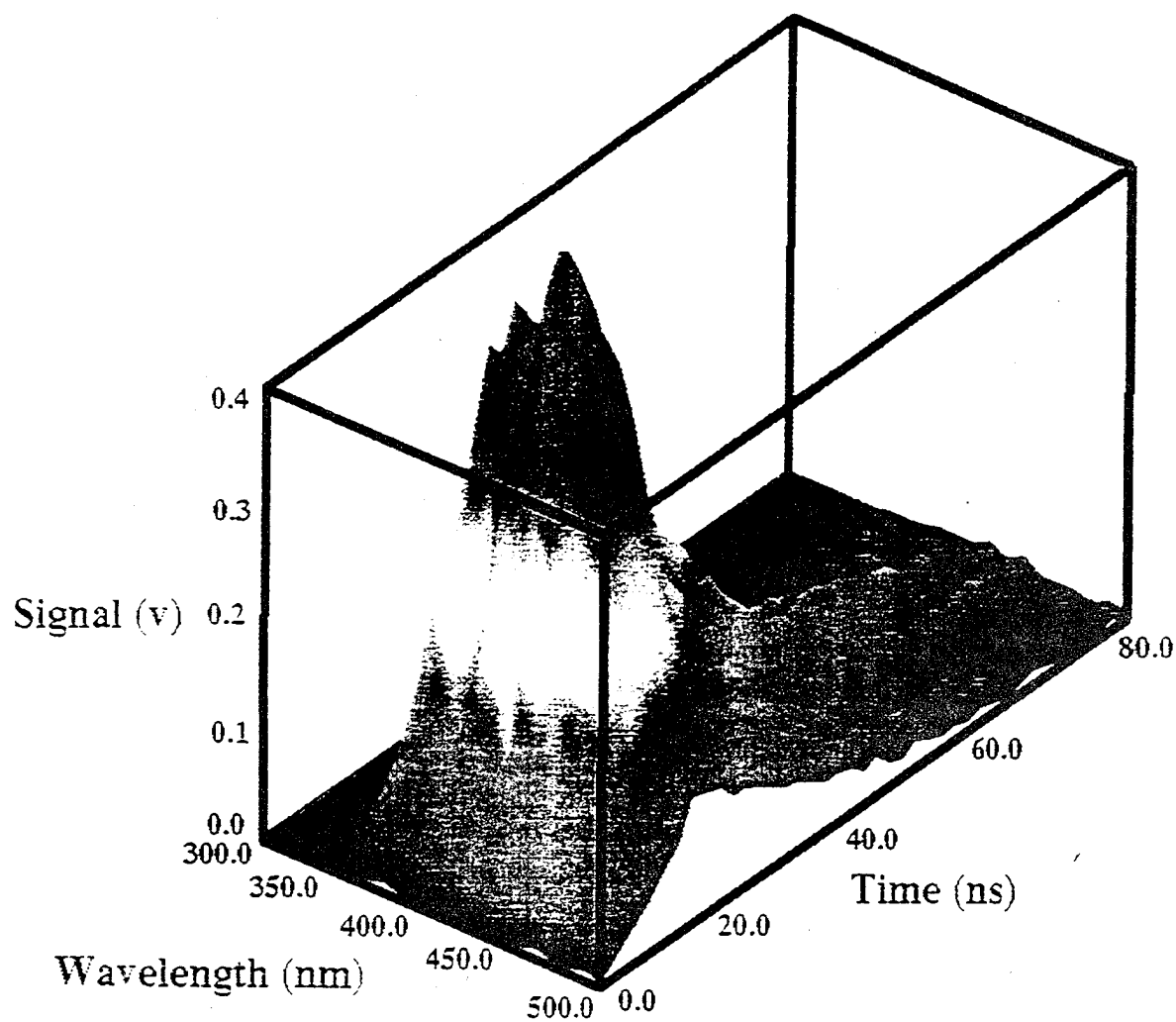


Figure 25. WTM at the North Tank Area.

Fuel Purge Area
FPA-03, Depth = 6.02 ft

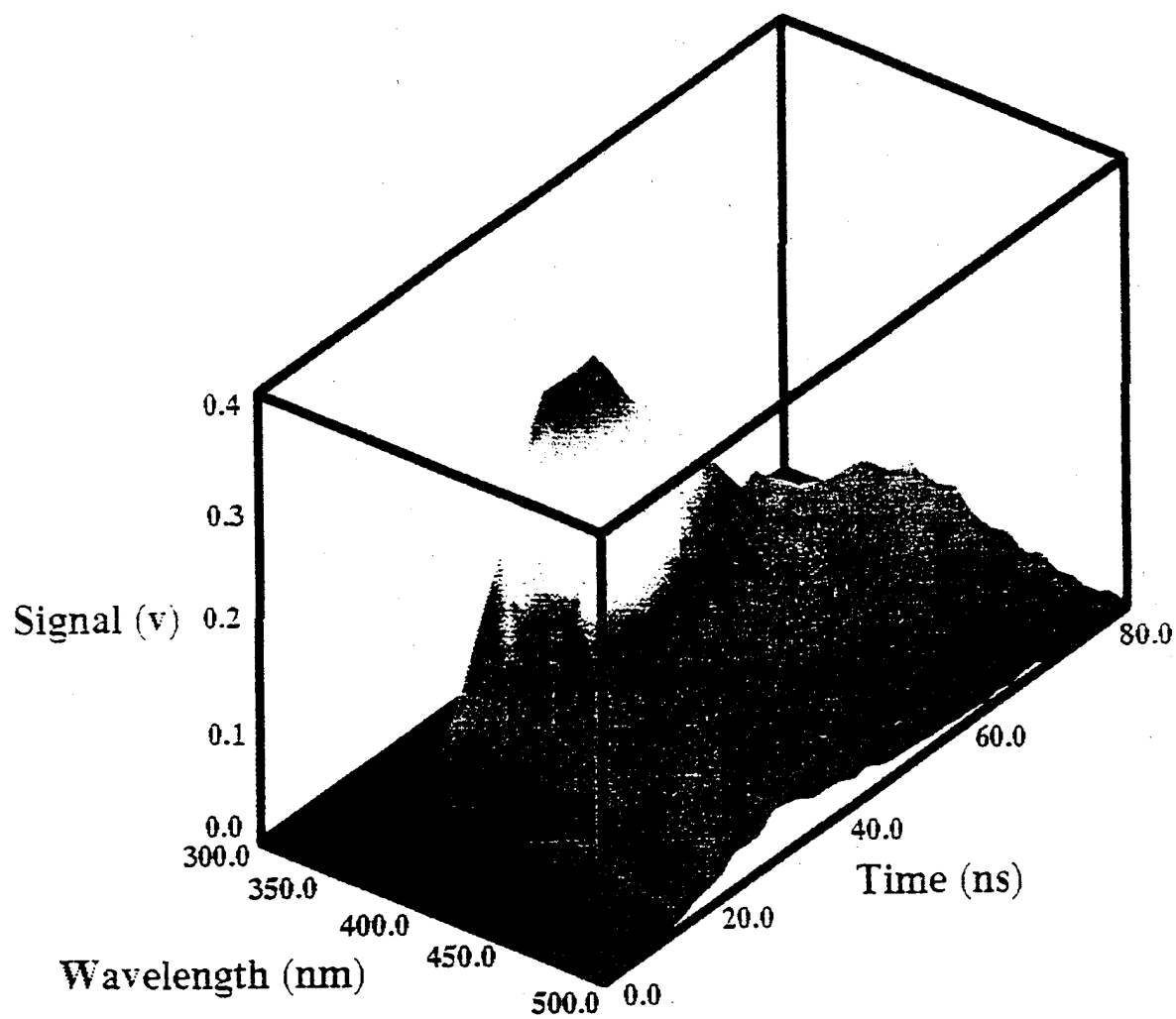


Figure 26. WTM at the Fuel Purge Area.

Fire Training Area
FTA-01, Depth = 3.47 ft

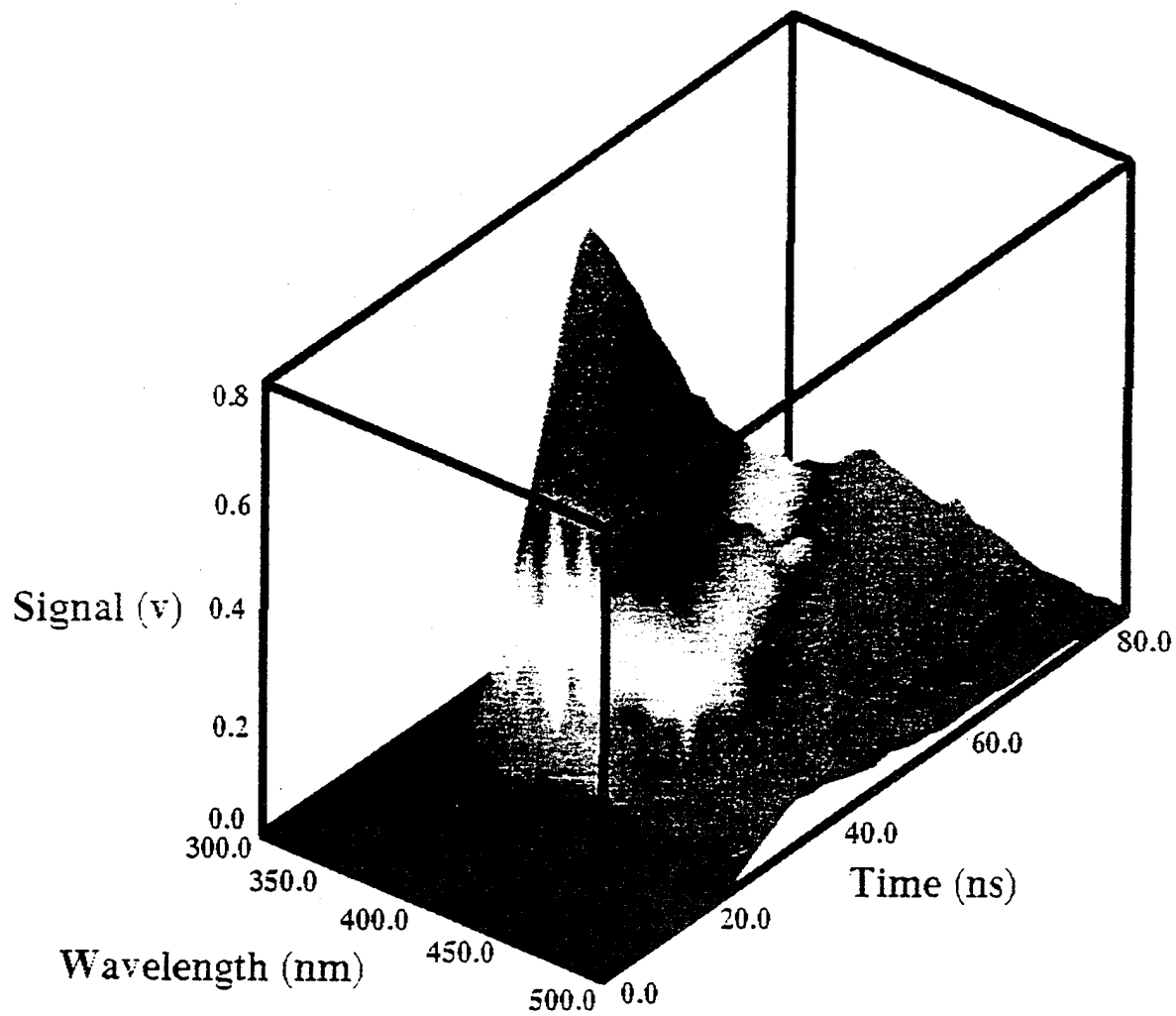


Figure 27. WTM at the Fire Training Area.

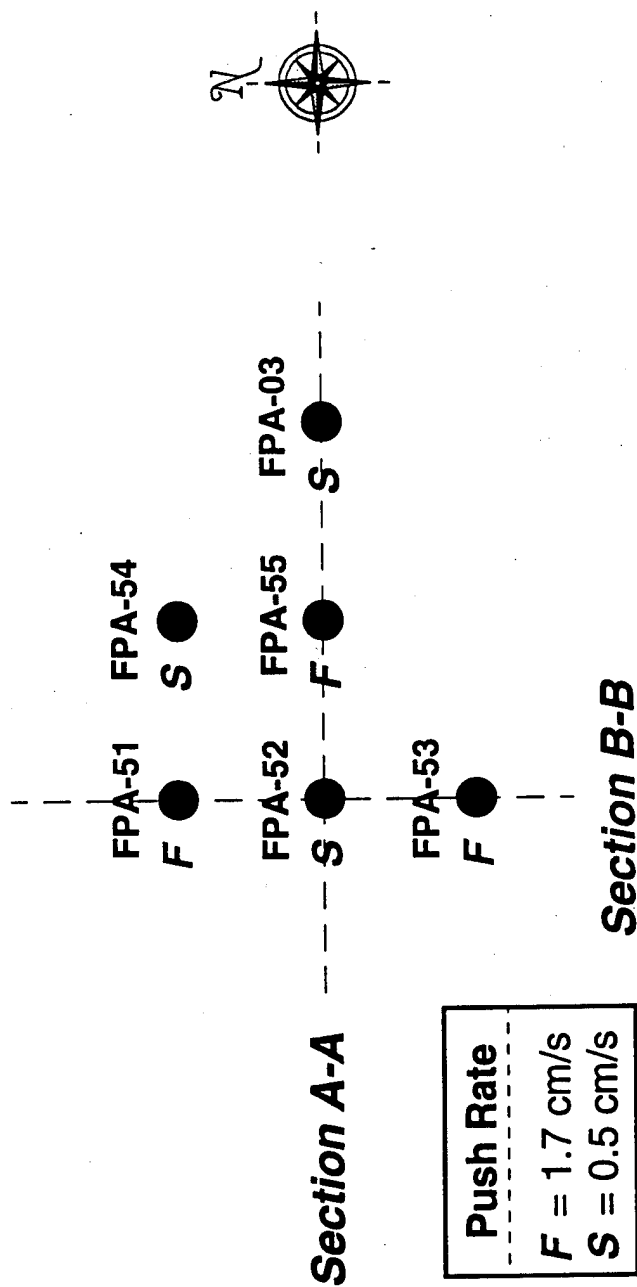


Figure 28. Layout of LIF Repeatability Series Test on 30-Inch Spacing

Tip Stress Along Section A-A

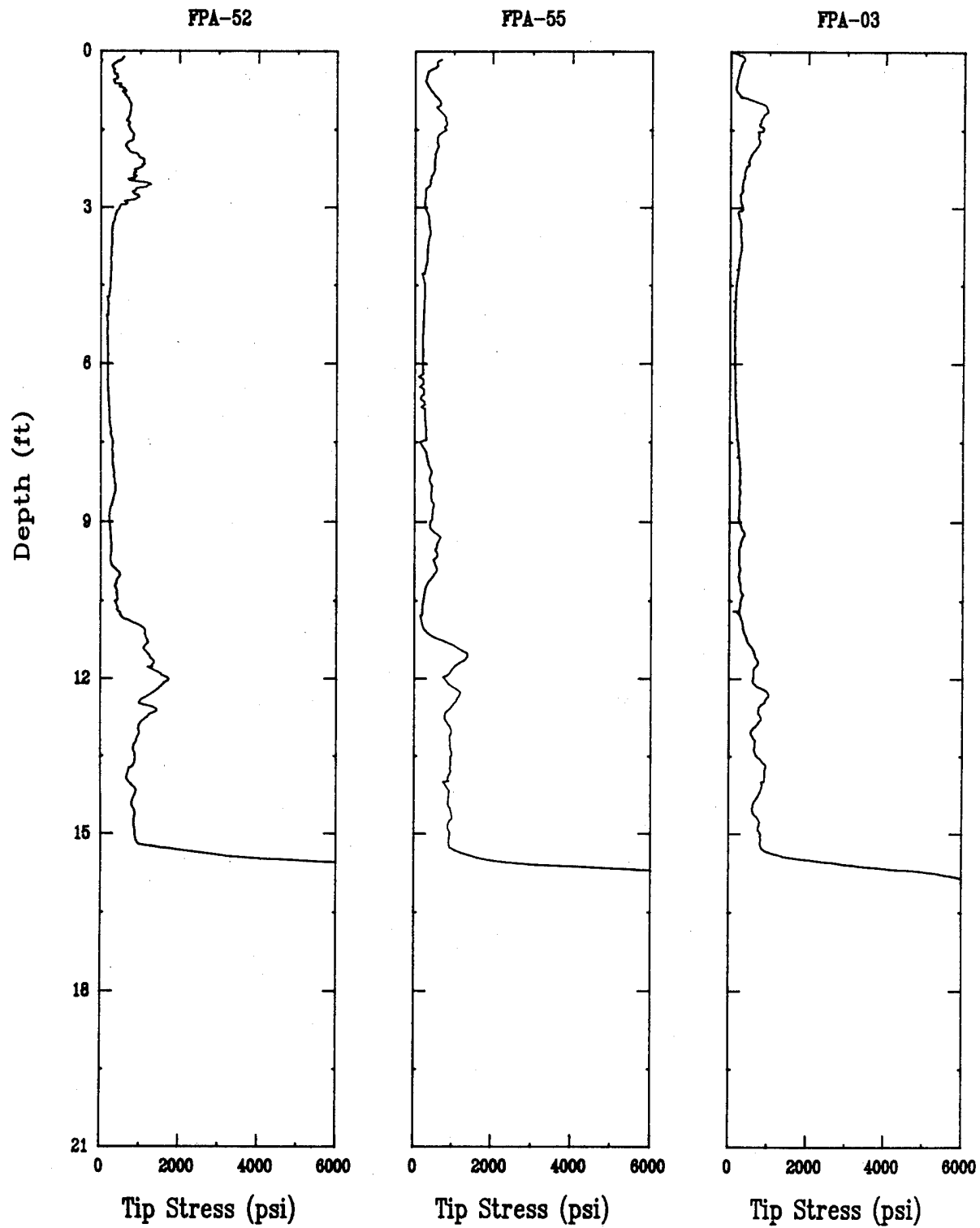


Figure 29. Tip Stress Profiles Along Section A-A of the Experimental Series Showing No Push Rate Effects on the Tip.

Figure 30 presents the sleeve stress profiles along the same section, which shows higher sleeve stresses for the profiles conducted at the slow rate than the profile conducted at the faster rate. The pore pressure responses were difficult to evaluate, but in general, the slower push rate generated additional pore pressures (see Figure 31).

Comparison of baseline corrected LIF measurements conducted at different penetration rates are plotted in Figure 32. The data plots present the corrected (baseline subtraction) LIF measurement, when applicable. As discussed above, baseline subtraction was used to reduce many of the day-to-day variances present in the LIF signals. The comparisons seem to indicate that push rate has little effect on the LIF responses, except for the vertical resolution of the data. FPA-55 has much lower resolution since the test was conducted at a faster push rate. It is interesting to note the FPA-55 also has a higher baseline than the other two tests.

Additional operating procedures that need to be evaluated are temperature effects on the consistency and stability of the laser light source. Each of these parameters need to be evaluated in relation to the impact they have on the measured LIF response to a given standard.

G. ONSITE DATA ANALYSIS AND SCIENTIFIC VISUALIZATION

Environmental site characterization is greatly enhanced by the ability to perform real-time, onsite analysis of test data. A major field program produces large amounts of data from various sources and in various forms. Convenient and flexible storage, retrieval and manipulation of the data are required to provide optimal and timely analysis. In parallel with the database problem is the need for multi-dimensional graphical display of data to aid in analysis and decision-making.

Using data generated from the LIF-CPT system, the above objectives were achieved during the field program. ARA's CPT systems have on-board data processing and graphics hardware that were used to observe uncorrected tip stress, sleeve stress, pore pressure and LIF profiles in real-time. For the Fuel Purge Area and the North Tank Area, the CPT and LIF data were used to guide subsequent sounding locations.

Sleeve Stress Along Section A-A

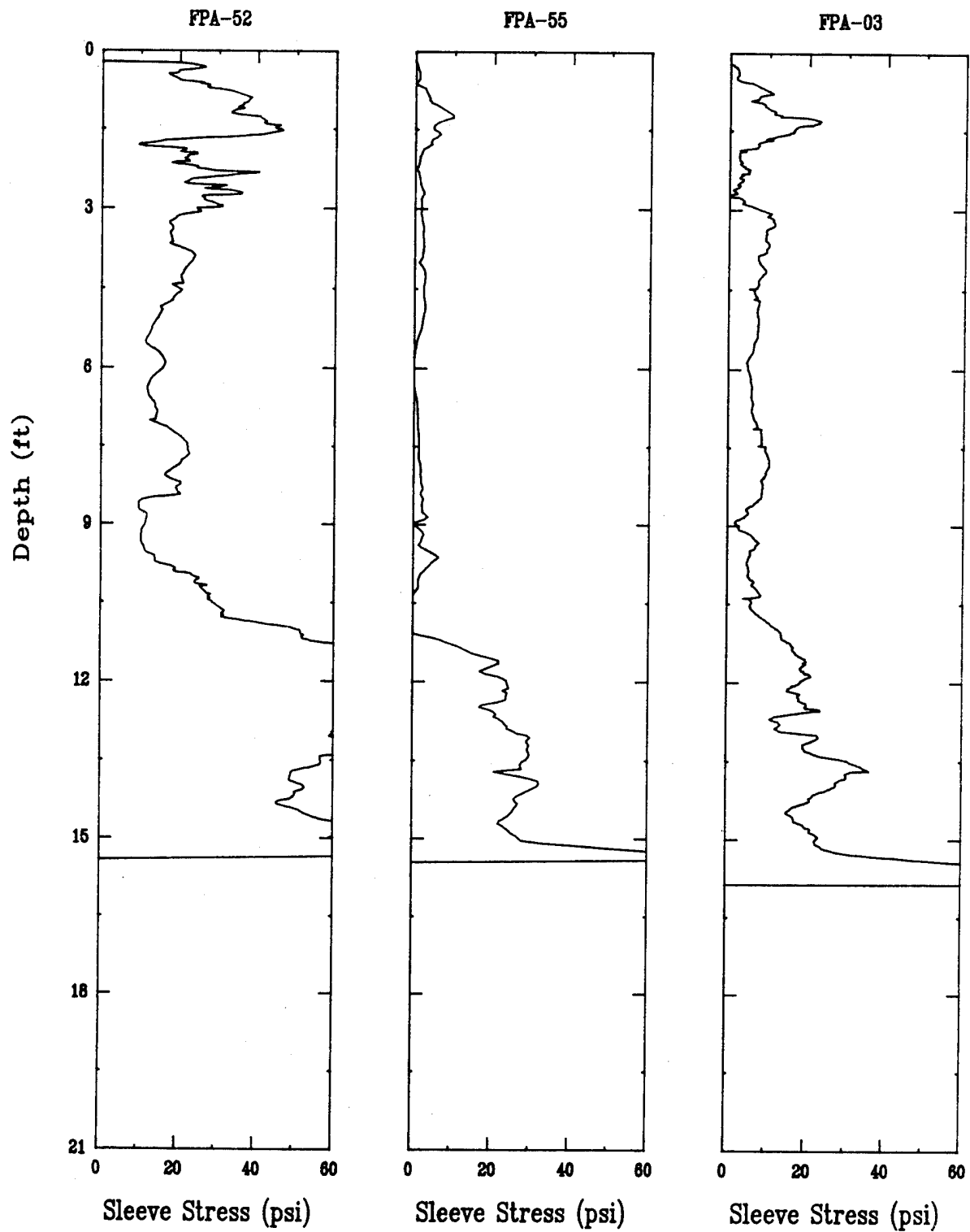


Figure 30. Sleeve Stress Profiles Along Section A-A of the Experimental Series Showing Increased Sleeve Stresses with Slower Push Rates.

Pore Pressure Along Section A-A

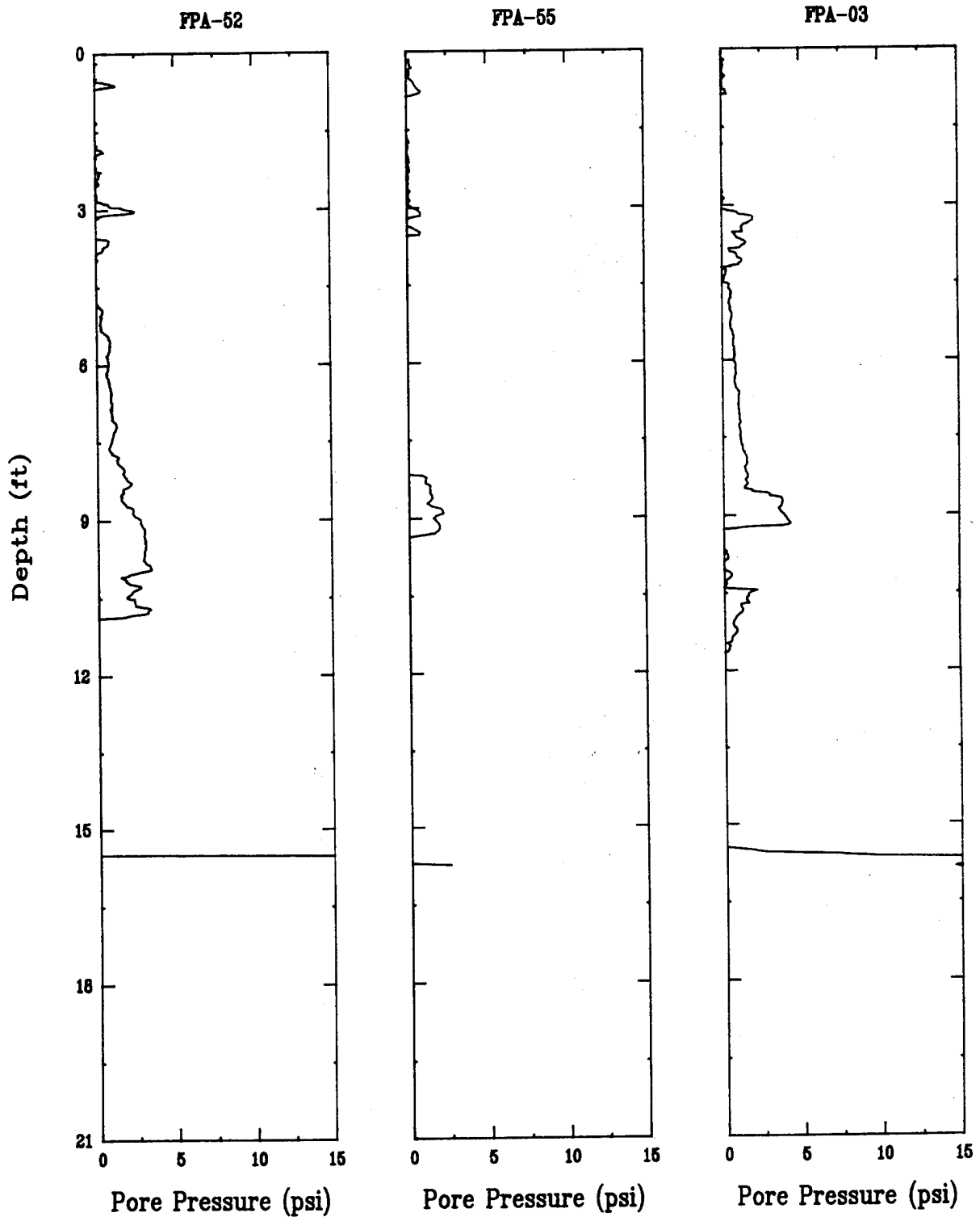


Figure 31. Pore Pressure Profiles Along Section A-A of the Experimental Series Showing Increased Pore Pressure Response with Slower Push Rates.

LIF Along Section A-A

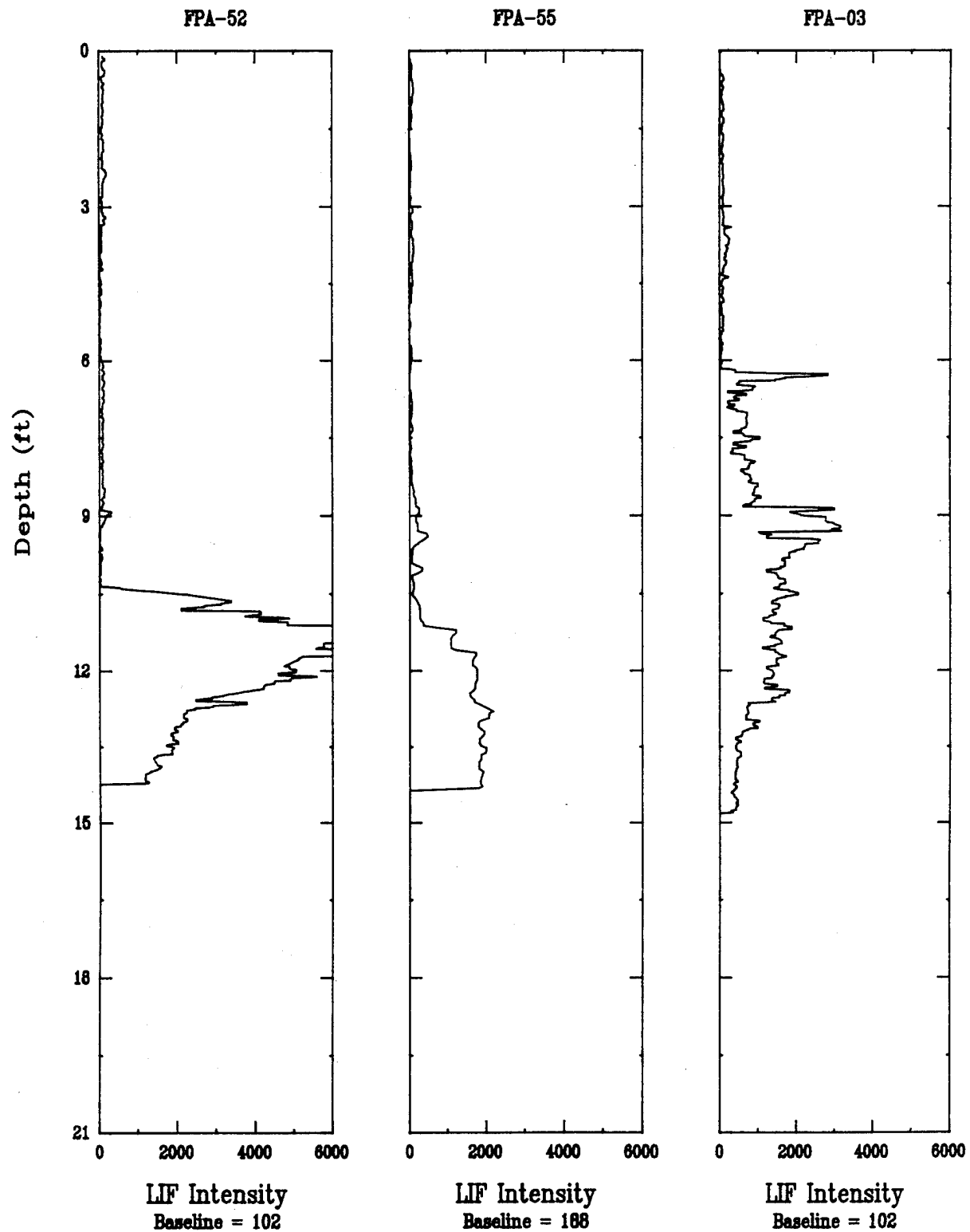


Figure 32. LIF Profiles Along Section A-A of the Experimental Series.

The main objective of the LIF-CPT onsite analysis was to use visual statistical models of the LIF data. To perform the database management and modeling, TECHBASE system was used. The system incorporates a relational database, a wide range of tools for analysis of stored data, geostatistical modeling, and graphics capability to display contours, cross-sections, perspectives, and vector drawings. Data profiles were transferred into TECHBASE using an acceptable data format; this required linking between a PC (CPT base computer) and a Silicon Graphics, Inc. Personal Iris workstation (TECHBASE and visualization computer) located in ARA's mobile laboratory. Site features information were digitized and imported in a similar manner.

Some trial statistical model runs were made to obtain satisfactory grid spacing, bounds, and search statistics. Advanced Visualization Systems, Inc.'s (AVS) scientific visualization package was used to display the model results and judge the quality of the data and statistics used. ARA developed a visualization program for geologic site characterization (GEOVIS) using standard AVS routines. Capabilities included cone/drill hole representation, surface features, volume bounds, volume rendering, isosurfaces, horizontal slicing, axes, and labeling. After initial debugging of the data processing sequence, visualization of the LIF-CPT data was performed within two to three days after acquisition. All aspects of visualization mentioned above (slicing, isosurfaces, etc.) were performed. Digitization of site features such as edge of pavement, buildings, etc. required additional time. This was the first demonstration of visualization of cone penetrometer data in the field.

The capabilities of the analysis system were used to determine the areal extent of a plume discovered during the testing at the FPA.

1. Plume Location and Delineation Using Onsite Three-Dimensional Graphics

Examination of surface conditions around FPA-11 indicated a filled area and stressed vegetation (see Figure 19). Additional probing with a shovel indicated that the filled area was comprised of a thin cover of clean sandy clay soil over possible petroleum-contaminated soils. The available evidence suggested that the contamination at FPA-11 was not due to the old ramp source, but possibly resulted from a separate spill.

With support from the Tinker AFB project coordinator, this hypothesis was tested using a more detailed site characterization strategy. LIF-CPT profiling was used to examine the lateral and vertical extent of soil contamination, with push locations determined by the real-time LIF results. Using onsite scientific visualization, the increased horizontal resolution allowed three-dimensional assessment of the problem area. This strategy was consistent with the AFSCAPS objective of presenting three-dimensional graphics of cone penetrometer data during the site characterization study.

Two main bodies of residual soil contamination are represented by the fluorescence slices shown in Figures 33 and 34. The visualization indicates that these main LIF highs are less than 40 feet wide, so that the CPT survey grid of 10 to 20 feet spacing was appropriate for that area. A separation of about 15 feet exists between the newly-discovered spill (western body) and the old ramp spillage (eastern body), suggesting their independent origin. A smaller body is located 40 feet south of the western body, and is centered near station FPA-20.

The geometry of the western contaminant body is indicative of a surface spill. High LIF values extend from near the surface to a depth of over 14 feet. Additionally, LIF values and chemical analyses of the shallow soils in the disturbed area suggest a spill contaminant source as well.

The vertical extent of this body is constrained by LIF data and corresponds to an elevation of 1,273 ft, or a depth of 12 feet. This depth is significant for several reasons. The CPT refusal layer, designated as the upper surface of the sandstone, is at 1,270 feet, MSL, whereas the perched water table is projected at 1,270 feet, MSL. Thus, the majority of residual product appears to remain in the lower unsaturated zone. The perched water table surface or low permeability conditions existing at the base of the residual soils (e.g., mineralization) may serve to restrict the fuel movement.

Visualization of the eastern body near the old ramp is not indicative of a surface spill, but this is probably a result of the following: 1) a larger grid spacing used in this area,

Fuel Purge Area
Elevation = 1282.0 ft

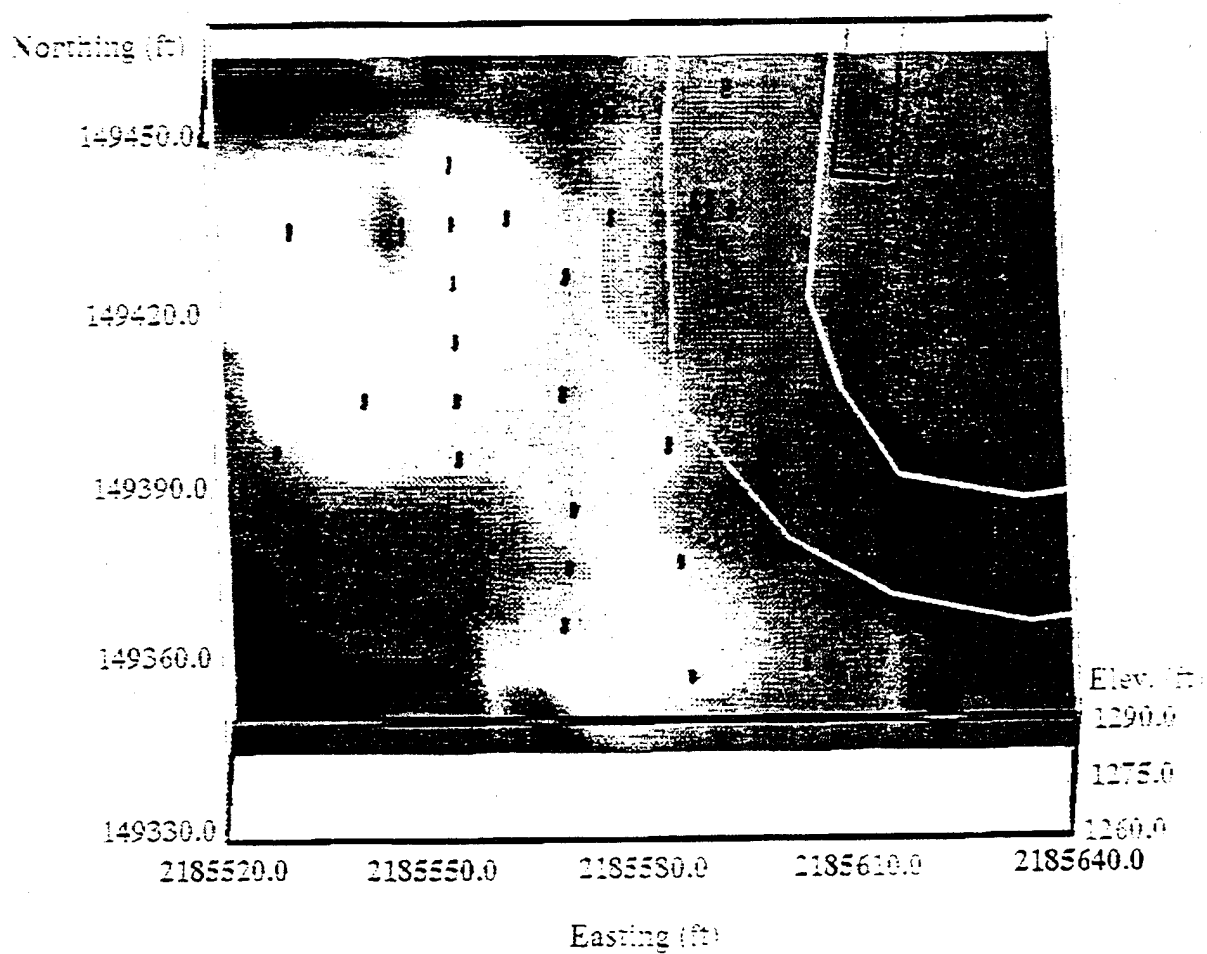


Figure 33. Visualization of Fuel Contamination at FPA at an Elevation of 1282.0 feet.

Fuel Purge Area
Elevation = 1277.5 ft

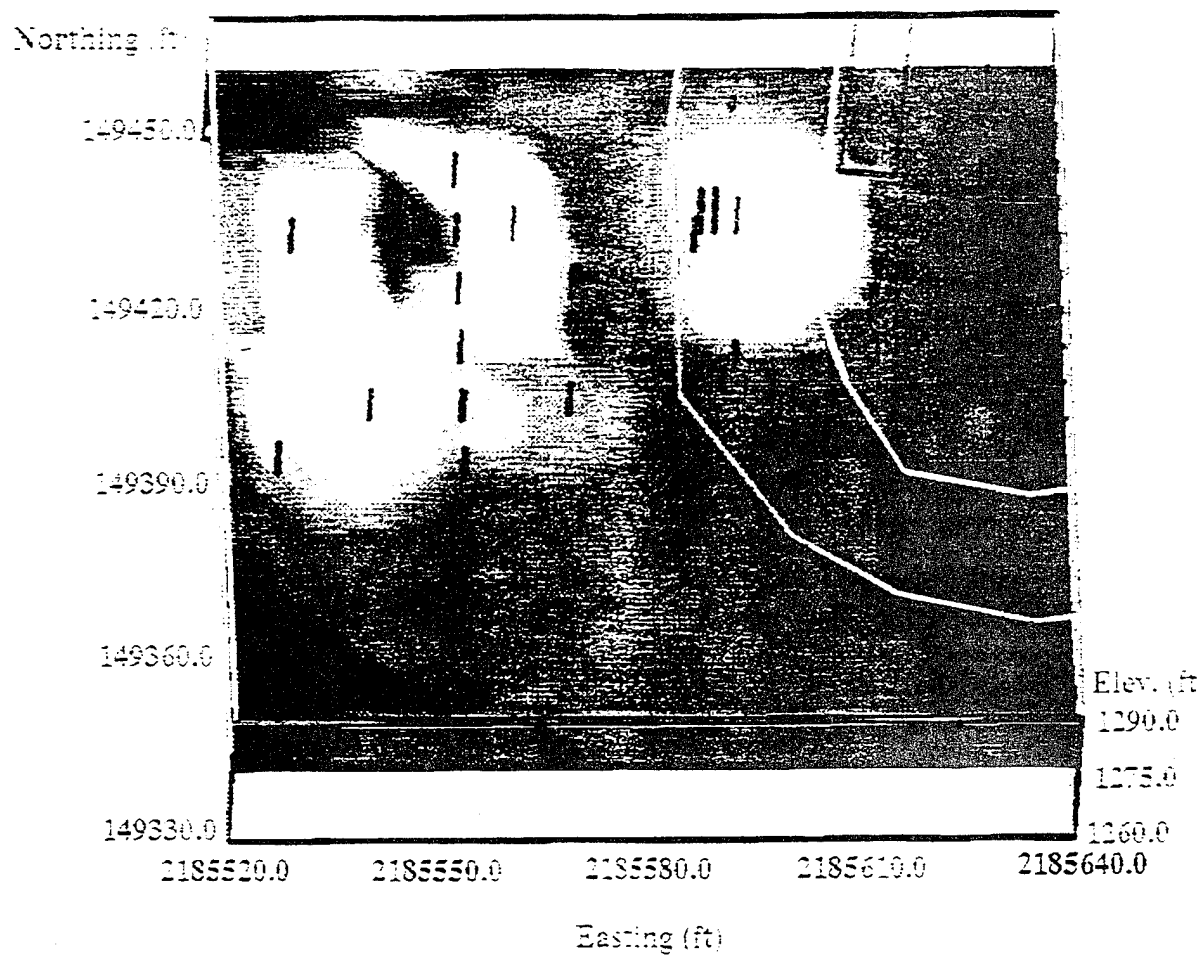


Figure 34. Visualization of Fuel Contamination at FPA at an Elevation of 1277.5 feet.

- 2) limitations posed by the concrete pad, i.e., fixed pavement core locations, and most probably,
- 3) removal of the most grossly-contaminated soils during dismantling of the old ramp.

H. COST/BENEFIT ANALYSIS OF DRILLING AND CPT PROBING

Studies for the Department of Energy have been completed that show the cost advantage of using CPT during site characterization (Reference 13). The greatest cost savings results from the optimization of the location of wells and overall reduction in number of wells achieved when using CPT surveys for geotechnical profiling and contaminant screening.

An analysis of the costs incurred in sampling by drilling versus sampling with the cone penetrometer also support a substantial cost savings in using cone penetrometer as a sampling probe. Comparison of the drilling costs and LIF-CPT cost incurred during the Tinker Demonstration are compared in Table 3. These are compared to ARA's standard CPT sampling costs for the same footage production rate. Cost for the LIF system were estimated and depreciated over a five-year period. These costs include an LIF technician. Drilling shows a cost of almost twice the CPT rate. About 50 percent of the price difference is due to costs associated with the handling, storage and disposal of drilling waste required at the Tinker sites. Drilling has the advantage of obtaining larger sample volumes and being able to penetrate through soft rock more easily. However, drill samples may have poor recovery, thereby providing poor depth information.

TABLE 3. COMPARISON OF CPT TO AUGER SAMPLING AT TINKER AFB

Augering - Actual			CPT - Estimated			
Item	No. Units	Unit Cost	Total Cost	No. Units	Unit Cost	Total Cost
Drilling/CPT	577 ft	\$111/ft	\$6,347	577 ft	\$13/ft	\$7,501
Grouting	577 ft	\$2.50/ft	\$1,442	577 ft	\$2.50/ft	\$1,442
Geologist	9 days	\$500/day	\$4,500	Not Required	\$0	\$0
Decon	17 hr	\$80/hr	\$1,360	4 hr	\$250/hr	\$1,000
Drum Purchase/Staging	21 drums	\$60/drum	\$1,200	N/A	\$60/drum	\$0
Drum Transfer	Lump Sum	\$400	\$ 400	N/A	\$0	\$0
TCLP Testing	5 tests	\$655/test	\$3,275	N/A	\$655/test	\$0
Waste Management	Lump Sum	\$4440*	\$4,440	N/A	\$0	\$0
Total			\$23,024			\$9,943
per foot			\$39.90			\$17.23

* Assuming waste is not categorized as a special waste or a hazardous waste.

SECTION VI

CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

1. AFSCAPS LIF-CPT Technology

Field evaluation of the AFSCAPS at Tinker AFB demonstrated that the combination of a LIF-CPT, onsite analytical laboratory, and onsite three-dimensional visualization can provide more detailed and timely (near real time) mapping of fuel contamination than can be accomplished by conventional drilling and sampling programs. The LIF-CPT can provide a continuous profile of the contaminant location and relative concentration with detection levels to at least the regulatory limits for TPH, and with further development detection below these limits can be achieved. Onsite analysis and visualization results in a field investigation program that can be adapted quickly to characterize unexpected plumes and to actively delineate the extent of the contaminant in three dimensions.

The LIF-CPT system is quite promising and sufficiently developed to be used as a field-screening tool. The LIF-CPT must be used with care and by experienced users of the LIF and CPT system. Interpretation of the soil stratigraphy has a strong influence on determination of LIF response, since LIF response is a function of soil type. The LIF-CPT system that is currently in the development phase is one of the most promising techniques for acquiring the detailed data required to produce accurate three-dimensional graphic representations of site contamination. Development of realistic, cost-effective remediation plans require the data density delivered by the LIF-CPT probe. However, because the technique has only recently been developed, the accuracy and precision of the technique cannot be determined until a sufficient number of well-characterized sites in a variety of geologic settings have been investigated. These investigations need to be conducted with sufficient analytical laboratory testing support to build a database that can be used to evaluate the precision and bias of the LIF-CPT probe.

The primary limitation in determining the precision, bias and accuracy of the LIF-CPT probe is developing calibration standards at the limits of interest to regulators. In developing these standards, the influence of soil type, sampling interval, and spatial variation on the contaminant concentration and distribution must be well documented. The LIF-CPT data indicates that the distribution can be quite variable in both the horizontal and vertical direction. Therefore, using standard sampling depth intervals is inadequate for developing correlations to the LIF data since these plans have a high probability of missing areas of contamination that are clearly shown on the LIF-CPT data. Calibration of the LIF-CPT probe using field-derived chemical data requires detailed characterization of the depth intervals to be used in developing the correlation; only areas of low variability as determined by the LIF-CPT probe should be used to develop the field calibration factors. At this stage of development, field correlations of LIF intensity to contaminant concentration are preferred because the effects of in situ degradation of the contaminant, soil type, moisture content and humic acids are all included in the correlation. The effect of these variables on LIF is not well understood, and any laboratory calibration factors that do not contain this influence will be highly uncertain.

2. Laboratory and Field Evaluation

The general lack of background research in the area of fluorescence spectroscopy applied to fuel-contaminated soils produced unanticipated results in the laboratory and field testing. Subsequently, deviations from the original test plans were made. Additional laboratory and field tests are recommended in further evaluations of the LIF-CPT probe. Results obtained from the prototype system indicate that fiber optic spectroscopy has great potential as a qualitative and quantitative field screening tool for hydrocarbon-contaminated soils.

The following main conclusions summarize the results from the laboratory and field evaluations:

1. Bending losses in the fiber associated with using the NDSU laser spectrometer and 6-around-1 fiber optic probe are not significant, except at the probe end. At the probe end, the fibers are bent 90 degrees in a 1.25-inch radius, creating high bending stresses. While the

fibers did not break, the high mechanical stresses caused the glass fibers to separate from the nylon jacket and to move relative to the focal plane. Over time this relative motion increased the measurement baseline to unacceptable levels.

2. The spectra of JP-4 and JP-5 are so similar that there appears to be little chance of distinguishing them by simple experiments. The WTM's of jet fuel and heating oil were different, with the heating oil fluorescence being greater at the longer wavelengths.

3. The fluorescence of naphthalene, methyl-naphthalene, or some chemically similar PAHs dominate the emission spectra of the subject fuels for excitation in the ultraviolet region shorter than 300 nm. For continuous cone penetrometer pushes, the optimal excitation wavelength is 280-290 nm or shorter. Not only do the fuels yield the greatest emission intensity for excitation in this region, but this is also the wavelength of maximum transmitted laser power. Work still remains to be conducted with the 266 nm laser source to evaluate the field utility of the 266 excitation wavelength.

4. The variation in the fluorescence spectral distribution as a function of environment (neat, dissolved, on soil) is important. BTEX-like emission is present for water saturated with fuel, but not for neat fuels or fuel-soil mixtures. This is consistent with the increased solubility of BTEX compared to other aromatics in the fuel. There is also a shift to higher emission spectrum (about 10 nm) for fuel-contaminated soils. In addition, relative intensity of the emissions as a function of environment has yet to be established.

5. Humic acids' contribution to LIF in soils (and ground water?) play an important role in the long wavelength fluorescence spectral distribution. The fluorescence of fuel loaded on soil is enhanced by the humic acids for emission wavelengths longer than 350 nm, possibly exceeding the contribution of the fuel components. Fuel is believed to act as a solvent, releasing additional humic acid, which is a strong source of fluorescence.

6. Laboratory analysis of fuels with the clayey soils is complicated by both the preparation of the fuel-soils mixture (clodding causing poor mixing) and in the role clays play

in absorption of organic (preferential uptake of fuel components and possible release of humic acids). Handling and residence time in preparation of fuel-soil mixtures also creates a source of uncertainty in the fluorescence results.

7. Compression of soil about the cone penetrometer probably creates measurable increases in LIF values due to reduction of voids and increase in moisture content. However, the results of the compression testing gained from the laboratory validation testing is inconclusive.

B. RECOMMENDATIONS FOR FUTURE WORK

A two-pronged approach is recommended for the next development phase for the LIF-CPT. One aspect should be the continuation of the field studies to provide a database for further evaluation of the LIF-CPT probe in a wider range of geologic settings and to provide Air Force environmental officers with information about the technology at their sites. The other aspect will be improvements in instrumentation, laboratory and field methods in order to establish to the satisfaction of EPA and other regulators the bias, reproducibility, error of the LIF-CPT system. The following addresses the recommendations for the LIF-CPT system derived from the laboratory and field evaluation program.

The first recommendation is the development of standard laboratory calibration and testing procedures. It has been demonstrated that the LIF response of fuel-contaminated soils is highly variable, depending on the soil type, soil moisture, fuel age, etc. The experience on this project is that detailed laboratory calibration and testing procedures are required. In addition, standard normalization techniques are required for presentation of the LIF data. The strength of the LIF emission is dependant on laser excitation and losses at the probe, both of which must be incorporated in the calibration procedures.

The prototype LIF system performed well in the field, but for widespread use by the environmental community several improvements in both the system hardware and software are required. Areas requiring additional work include:

- Higher repetition rate laser (50 Hz) for faster data acquisition,
- Improved mounting of fiber to eliminate pistoning effect,
- Miniaturization of laser system,
- Incorporation of CCD sensors to provide both time and spectral data,
- Better environmental (climate and shock isolation) control of laser system, and
- Developing advanced data analysis methods to include chemical identification.

The ability to perform rapid and inexpensive analyses in the field and make onsite decisions with regard to site characterization strategies in a routine manner may be realized with advancement of AFSCAPS technologies. In addition to the LIF-CPT system, the AFSCAPS system should be expanded to incorporate recent research being conducted both by the Air Force and DOE in the areas of sensors, remediation and data analysis methods. These include:

- Incorporate onsite geostatistical models with existing methods which incorporate contaminant fate and transport models to gain better understanding of site characteristics
- Develop additional sensors such as the DOE-developed TCE sensors, and sensors for determining geotechnical and chemical properties of interest including soil Ph, oxygen content, and soil moisture, etc.
- Use cone penetrometer systems to install and/or perform ground water and soil monitoring at remediation sites.
- Develop remedial technologies which implement and take advantage of the minimally invasive cone penetrometer technology.

APPENDIX A
PARTIAL PARTS LIST FOR THE LASER SPECTROMETER SYSTEM

TABLE A-1. PARTIAL PARTS LIST FOR THE LASER SPECTROMETER SYSTEM

<u>EQUIPMENT</u>	<u>Part #</u>	<u>Unit Price</u>	<u>Price</u>
Rocky Mountain Instruments			
1501 S. Sunset Street, Colorado 80501 303-651-2211			
<u>HIGH POWER MIRRORS</u>			
2 ea. 532nm 100% at 0 deg	PM-2506-Q+HPM053	\$165	\$330
1 ea. 355nm 100% at 0 deg	PM-2506-Q+HPM036	\$165	\$165
<u>PARTIAL REFLECTORS</u>			
1 ea. 532nm R=80% @ 45 deg S polarization	WI-2506-Q+PAR053(80%)(45S)	\$240	
1 ea. 355nm R=70% @ 45 deg S polarization	WI-2506-Q+PAR 036(70%)(45S)	\$275	
Esco Products Inc.			
171 Oak Ridge Road			
Oak Ridge, New Jersey 07438-0155 201-697-3700			
<u>PRISMS</u>			
4 ea. 15 mm S1-UV 90	I115150	\$ 64	\$256
<u>LENSES</u>			
2 ea. 1" x 4" focal length	A110040	\$ 82	\$164
<u>DYE CELL PARTS</u>			
6 ea. S1-UV 20mm 90° Prism	I 120 200	\$ 90	\$540
12 ea. S1-UV 1/2" X 1/16" DISK	P105063	\$ 6.80	\$ 82
12 ea. S1-UV 1/2" X 1/8" DISK	P605125	\$ 3.50	\$ 42
<u>Sapphire Window</u>			
2 ea. 3/8" dia. x 0.08" thick UV grade	G103-080	\$13	\$26
Newport Corporation			
P.O. Box 8020			
Mt. Baldy Circle			
Fountain Valley, CA 92728-8020 714-963-9811			
<u>DYE LASER MIRRORS</u>			
2 ea. 1/2" x 0.122" Mirrors	05D20BD.1	\$ 67	\$134
2 ea. 1" x 0.236" Mirrors	10D20BD.1	\$ 96	\$192

**TABLE A-1. PARTIAL PARTS LIST FOR THE LASER SPECTROMETER
SYSTEM (CONTINUED).**

OPTICS POSITIONERS

3 ea. Fiber Optic Positioners	FP-2	\$302	\$904
4 ea. Lens Mounts	LM-1		
ea. Beamsplitter Mounts	MM2-1A	\$51.60	\$361
10 ea. Mirror and Prism Mounts	MM2	\$49	\$490

GOGGLES

2 ea. Laser Goggles	G-LGS-A-NGDA	\$298	\$596
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ROTATION STAGES

2 ea. Solid Insert Hi-Res Rotation St.	471	\$610	\$1,220
2 ea. Apertured Hi-Res Rotation St.	471-A	\$665	\$1,330

**Edmund Scientific Company
101 E. Gloucester Pike
Barrington, NJ 08007-1380 609-573-6250**

GRATINGS

2 12.5 x 25mm Gratings 1800 grooves/mm VIS	A43,221	\$ 63	\$126
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Spectra Physics

PRISM

1 ea. Pellin-Broca Dispersion			?
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**Ferranti Venus Inc.
399 Smith St.
Farmingdale, NY 11753**

HIGH VOLTAGE POWER SUPPLIES

2 ea. -300 to -3000 Volt Supplies	LR-3N	\$263	\$526
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**Interactive Radiation (INRAD)
181 Legrand Av.
Northvale, NJ 07647**

DOUBLING CRYSTALS

1 R6G KDP CRYs in Cell	541-120 R6G CUT	\$1150	
1 C500 KDP CRYs in Cell	541-120 B1 CUT	\$1150	

**TABLE A-1. PARTIAL PARTS LIST FOR THE LASER SPECTROMETER
SYSTEM (CONTINUED).**

Schott Glass Technology

VISIBLE BLOCKING FILTERS

2 ea. 50mm x 50mm x 3mm VIS Filters	UG-5	2 x	\$57	\$104
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Technical Manufacturing Company

15 Centennial Drive

Peabody, MA 01960 800-542-9725

OPTICAL BREADBOARD

1 ea. 30" x 48" x 4" Optical Breadboard	77-231-02		\$1165	
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Walter Norris Company

Chicago, Illinois 708-671-7410

AIR CUSHIONS

4 ea. Air Cushions	1B5-500		\$ 76.91	\$308
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United Motions

2954 Scott BLVD.

Santa Clara, CA 95054 408-970-9742

STEPPER CONTROLLER

1 ea. CYB55B Motion Controller	NMA-4S		\$200	
4 ea. SMD 2.0 Driver Packs	QDHLCI	4 x	\$200	\$800

Cole Parmer

7425 North Oak Park Avenue

Chicago, Illinois 60648 800-323-4340

DYE CELL PUMPS

2 ea. Centrifugal Pumps	L-07021-00	2 x	\$85	\$170
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**TABLE A-1. PARTIAL PARTS LIST FOR THE LASER SPECTROMETER
SYSTEM (CONTINUED).**

Thorn EMI Electron Tubes Limited
100 Forge Way, Unit F
Rockaway, NJ 07866
Telephone: (201)-586-9594
FAX: (201)-586-9771

1 ea. phototube	9813QB	\$995
1 ea. housing	B2F-RFI	\$610

Spectra Physics Lasers Inc.
255 Old New Brunswick Rd.
Suite 40
Piscataway, NJ 08854-4174
Telephone: (800)-631-5693
FAX: (201)-981-0029

1 ea. Nd:YAG laser	GCR-12-S	\$21,520*
1 ea. Harmonic generator	HG-2C	\$8,032*

*Prices represent 15% discount (per Ralph Swaine) and 5% PATLEX discount on laser.
 Laser is to be used for government supported (Air Force) contract.

Tektronix Inc.
2685 Long Lake Road
Roseville, MN 55113
Telephone: (612)-635-0520
FAX: (612)-635-0716

1 ea. digital oscilloscope	\$2,440	\$7,990
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Spex Industries, Inc.
3880 Park Avenue
Edison, N. J. 08820
Telephone: (800)-438-7739
FAX: (908)-549-5125

1 ea. spectrometer	270M	\$3,600
1 ea. computer controlled exit slit		\$625
1 ea. motorized swingaway mirror		\$870
1 ea. computer controlled dual grating turret		\$1,000

**TABLE A-1. PARTIAL PARTS LIST FOR THE LASER SPECTROMETER
SYSTEM (CONCLUDED).**

1 ea. 1200 grooves/mm grating, blaze 250 nm	\$600
1 ea. 1200 grooves/mm grating, blaze 500 nm	\$600
Total	\$7,890

MACHINE SHOP PARTS

15 Lens and Prism Posts and Forks (Minimum)	
4 Dye Cell Posts and Forks (Adjustable with machined MM2s)	
4 Mounts for Rotation Stages (Design Unknown)	
6 Nylatron Cell Flanges	REUBEN \$840

Fiberguide Industries
1 Bay St.
Stirling, NJ 07980 (908) 647-6601

FIBER OPTICS

1,000 meters 600 micron PCS	SPC600N	\$3.40	\$3,400
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Dell Computer

<u>Laser Spectrometer Control Computer</u>	
486 Computer, 4M RAM, 200 M HD	\$2,918.00
ATI Graphics Card	\$299.00

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